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External Review Draft. Volume 2

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Volume II of V

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Data on health and welfare effects are emphasized, but additional information is provided for understanding the nature of the oxidant pollution problem and for evaluating the reliability of effects data as well as their relevance to potential exposures to ozone and other photochemical oxidants at concentrations occurring in ambient air. Separate chapters are presented on the following exposure-related topics pertaining to ozone and other photochemical oxidants: properties, chemistry, and measurement; concentrations typically found in ambient air; formation and transport once formed; and nature, source, measurement, and concentrations of precursors.

The specific areas addressed by chapters on health and welfare effects are: the toxicological appraisal of effects of ozone and other oxidants; effects observed in controlled, human exposures; effects observed in field and epidemiological studies; effects on vegetation seen in field and controlled exposures; effects on natural and agroecosystems; and effects on nonbiological materials observed in field and chamber studies.

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LIST OF ABBREVIATIONS AND SYMBOLS

~	approximately
λ	wavelength
AFR	air:fuel ratio
APHA	American Public Health Association
aq	aqueous
ASL	above sea level
atm	atmosphere
avg	average
b.p.	boiling point
bz	benzene
C	carbon
°C	degrees Celsius
CA	chromotropic acid
CAMP	Continuous Air Monitoring Program
CARB	California Air Resources Board
cc	cubic centimeter
CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
cm	centimeter
concn	concentration
DBH	tree diameter at breast height
DNPH	2,4-dinitrophenylhydrazine
DOT	Department of Transportation
E_0	normal electrode potential
ECD	electron-capture detector
EKMA	Empirical Kinetic Modeling Approach
EPA	U.S. Environmental Protection Agency
FID	flame ionization detector
FRM	Federal Reference Method
ft	foot
FTIR	Fourier-transform infrared
g	gram(s)

LIST OF ABBREVIATIONS AND SYMBOLS (continued)

g/mi	grams per mile
GC	gas chromatography
GPT	gas-phase titration
hr	hour(s)
hv	photon
HC	hydrocarbons
HCN	hydrogen cyanide
HCOOH	formic acid
HFET	Highway Fuel Economy Driving Schedule
Hg	mercury
H_2O_2	hydrogen peroxide
HO_2	hydroperoxy
HONO	nitrous acid
$HONO_2$	nitric acid
HPLC	high-pressure liquid chromatography; also, high-performance liquid chromatography
HPPA	3-(p-hydroxyphenyl)propionic acid
HRP	horseradish peroxidase
H_2O	water
H_2SO_4	sulfuric acid
in	inch(es)
IR	infrared
k	constant
KI	potassium iodide
km	kilometer
L	liter(s)
LAAPCD	Los Angeles Air Pollution Control District
LCV	leuco crystal violet
ln	natural logarithm (base e)
LST	local standard time
M	molar
m	meter(s)
mb	millibar(s)

LIST OF ABBREVIATIONS AND SYMBOLS (continued)

MBTH	3-methyl-2-benzothiazolinone hydrazone
mg	milligram(s)
mg/m^3	milligrams per cubic meter
MGE	modified graphite electrode
min	minute(s)
ml	milliliter(s)
mm	millimeter(s)
mM	millimolar
MMC	mean meridional circulation
m.p.	melting point
mph	miles per hour
MS	mass spectrometry
MSL	mean sea level
MT	metric tons
MTBE	methyl tertiary butyl ether
NA	Not available
NAAQS	National Ambient Air Quality Standard
NADB	National Aerometric Data Bank
NAMS	National Aerometric Monitoring Stations
NAPBN	National Air Pollution Background Network
NAS	National Academy of Sciences
NBS	National Bureau of Standards
NECRMP	Northeast Corridor Regional Modeling Project
NEDS	National Emissions Data System
NEROS	Northeast Regional Oxidant Study
NH_3	ammonia
NH_4NO_3	ammonium nitrate
NF	National Forest
nm	nanometer
NMHC	nonmethane hydrocarbons
NMOC	nonmethane organic compounds
NO	nitric oxide
NO_x	nitrogen oxides

LIST OF ABBREVIATIONS AND SYMBOLS (continued)

NO_2	nitrogen dioxide
NO_3	nitrogen trioxide
N_2O	nitrous oxide
NR	natural rubber
NYCC	New York City Driving Schedule
O_2	oxygen
O_3	ozone
PAN	peroxyacetyl nitrate
PBzN	peroxybenzoyl nitrate
pH	reciprocal of H ion concentration
PNA	peroxynitric acid
PPN	peroxypropionyl nitrate
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PSD	Prevention of Significant Deterioration
psig	pounds per square inch gauge
PST	Pacific Standard Time
PUFA	polyunsaturated fatty acids
RAPS	Regional Air Pollution Study
RTI	Research Triangle Institute
S.D.	standard deviation
SAROAD	Storage and Retrieval of Aerometric Data
SBR	styrene-butadiene rubber
SCAB	South Coast Air Basin
sec	second(s)
SLAMS	State and Local Air Monitoring Stations
SMSA	Standard Metropolitan Statistical Area
SRM	Standard Reference Material
SSET	small-scale eddy transport
STA	seasonal tropopause adjustment
STP	standard temperature and pressure
SURE	Sulfate Regional Experiment Sites

LIST OF ABBREVIATIONS AND SYMBOLS (continued)

TEL	tetraethyl lead
Tenax GC	adsorbent used in NMOC analysis
TF	tropopause-folding events
tg/yr	teragrams per year
THC	total hydrocarbon
TML	tetramethyl lead
TNMHC	total nonmethane hydrocarbons
TWC	three-way catalyst
$\mu g/m^3$	microgram per cubic meter
μM	micromolar
U	uranium
UHAC	uranium hydroxamic acid chelates
U.S.	United States
UV	ultraviolet
V	vanadium
v/v	volume - volume
VHAC	vanadium hydroxamic acid chelates
VOC	volatile organic compounds
vol %	volume percent
w/w	weight - weight
WCOT	wall-coated open tubular (column)
XAD-2	absorbent used in NMOC analysis
XO	xylenol orange
yr	year(s)

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2. INTRODUCTION

2.1 PURPOSE AND LEGISLATIVE BASIS OF DOCUMENT

According to the Clean Air Act, the Administrator of the United States Environmental Protection Agency (EPA) is required to issue, and to revise on a periodic basis, air quality criteria for certain air pollutants specified in the Act. Among these are pollutants known as photochemical oxidants. The term "photochemical oxidants" has historically been defined as those atmospheric pollutants that are products of photochemical reactions and that are capable of oxidizing neutral iodide ions (U.S. Environmental Protection Agency, 1978). Research has unequivocally established that photochemical oxidants in ambient air consist mainly of ozone, peroxyacetyl nitrate, and nitrogen dioxide, and of considerably lesser amounts of other peroxyacyl nitrates, hydrogen peroxide, alkyl hydroperoxides, and nitric and nitrous acids. Other oxidants suspected to occur in ambient air in trace amounts include peracids and ozonides.

Although it is by definition a photochemical oxidant, nitrogen dioxide is not included among the oxidants discussed in this document. The formation of nitrogen dioxide clearly precedes the formation of ozone and related other oxidants in the ambient air. While nitrogen dioxide is the dominant oxidant early in the day, ozone and related other oxidants predominate from late morning or midday through much of the afternoon.

In addition to the differences in patterns of occurrence of nitrogen dioxide versus ozone and its related oxidants, nitrogen dioxide is known to exert deleterious effects on human health and welfare. The Clean Air Act specifies, therefore, that criteria be issued separately for nitrogen dioxide and other oxides of nitrogen. The second criteria document prepared by EPA on the oxides of nitrogen was published in 1982 (U.S. Environmental Protection Agency, 1982a). That document discussed nitric and nitrous oxides, nitrogen dioxide, nitric and nitrous acid, and nitrosamines.

The purpose of this document is to review and evaluate the scientific literature on ozone and related oxidants and to document their effects on public health and welfare. Such documentation provides the Agency with a scientific basis for deciding whether regulations controlling these pollutants are necessary and for deriving such ambient air quality standards as may be needed.

According to section 108 of the Clean Air Act, as amended in 1977, a criteria document shall

> ...accurately reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on public health or welfare which may be expected from the presence of such pollutant in the ambient air, in varying quantities.
>
> (Clean Air Act, U.S.C. §§7408 and 7409)

Air quality criteria may be defined, then, as qualitative and quantitative information that describes the effects of a pollutant on public health and welfare in terms of the respective exposures that elicited them.

This document is a revision of Air Quality Criteria for Ozone and Other Photochemical Oxidants (U.S. Environmental Protection Agency, 1978), as specified in sections 108 and 109 of the Clean Air Act. As used in this document, the term "photochemical oxidants" refers to ozone, the peroxyacyl nitrates, and hydrogen peroxide. The oxides of nitrogen are discussed, but only in the context of their role as precursors to ozone and related oxidants.

2.2 THE OXIDANT PROBLEM

As described in the Clean Air Act, criteria pollutants are those atmospheric pollutants that are ubiquitous and are emitted into the air from numerous and diverse sources. While ubiquitous, ozone and other photochemical oxidants are not emitted into the air as primary pollutants. Rather, they are formed as secondary pollutants in the atmosphere from ubiquitous primary organic and inorganic precursors that are emitted by a multiplicity of sources. Oxidant pollution is widespread in this country as the result of a combination of many factors, such as local meteorological conditions as well as the concentrations, composition, and patterns of occurrence of the primary pollutants that give rise to the oxidants.

An overview of the relationships among nitrogen oxides, volatile organic compounds such as hydrocarbons, and the respective photochemical ocidants is helpful for understanding material presented in later chapters. Figure 2-1 depicts the idealized patterns of the respective primary and secondary pollutants involved in atmospheric photochemical processes. Although derived from laboratory data, the pattern depicted in Figure 2-1 nevertheless represents the general pattern seen in ambient air, as field research has corroborated.

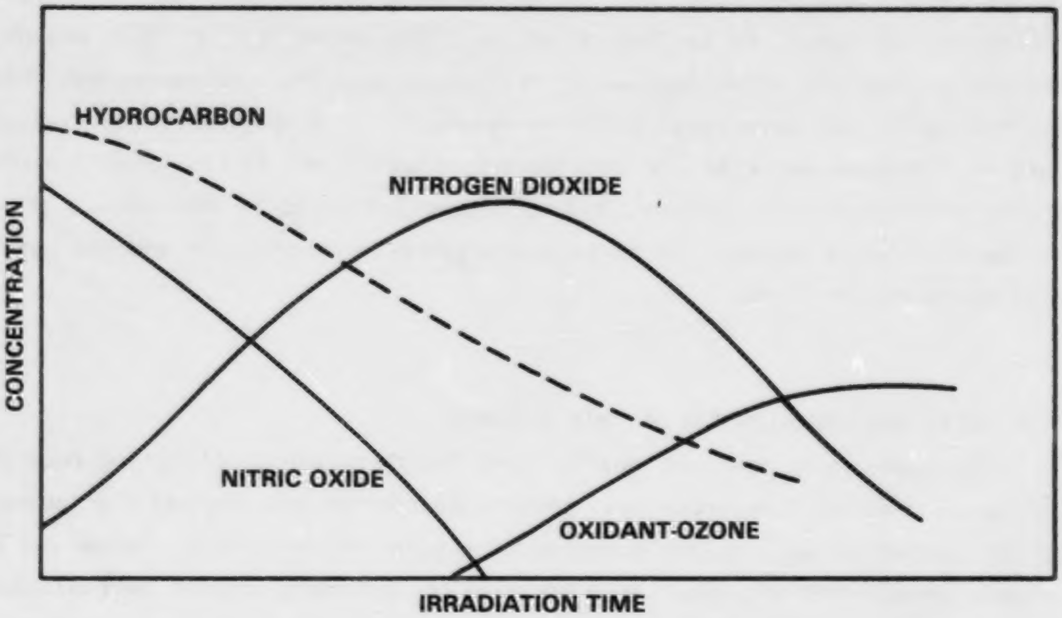

Figure 2-1. Chemical changes occurring during photoirradiation of hydrocarbon-nitrogen oxide-air systems.

Source: U.S. Environmental Protection Agency (1978).

Ozone is the photochemical oxidant currently regulated by national ambient air quality standards. It is well established that ozone produces effects on public health and welfare that are attributable to its characteristics as an oxidant. The bulk of health- and welfare-related research has centered on ozone, largely because it is the major photochemical oxidant found in ambient air. While data on the health and welfare effects of hydrogen peroxide and of the peroxyacyl nitrates are few, sufficient data on their effects and on their concentrations exist to be indicative of their potential, at high enough concentrations, for affecting public health and welfare. As subsequent chapters will document, the peroxyacyl nitrates appear to be ubiquitous. The available data on hydrogen peroxide are considerably fewer; from information on atmospheric photochemistry, however, hydrogen peroxide would be expected to occur, at least in trace amounts, in those atmospheres in which ozone and the peroxyacyl nitrates are found.

2.3 SCOPE AND ORGANIZATION OF THIS DOCUMENT

The atmosphere does not easily lend itself to the partitioning required for documentation. Nevertheless, certain boundaries are logical for purposes of discussion as well as for purposes of regulatory decisions. Ozone and its organic precursors are known to give rise to secondary organic aerosols (see chapter 5). Likewise, ozone and hydrogen peroxide both appear to participate in those atmospheric oxidations of nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) that lead to visibility degradation in the atmosphere and to the environmental phenomenon known as acidic deposition. The contributions of ozone and hydrogen peroxide to these atmospheric and environmental phenomena cannot at present be quantified, however. The Agency has chosen to discuss these topics in the air quality criteria documents on the oxides of nitrogen and on particulate matter and sulfur oxides (U.S. Environmental Protection Agency, 1982a, 1982b). The present document includes brief discussions of the atmospheric chemistry of ozone and hydrogen peroxide relative to these topics but does not include information on visibility degradation or on acidic deposition.

For ease of printing, distribution, and review, this document is being released in five volumes. The first volume contains the summary and conclusions for the entire document. The second contains the introduction to the document (chapter 2) and all chapters dealing with the precursors to photochemical oxidants (chapter 3); the formation of photochemical oxidants (chapter 4); their properties, reactions, and measurement once formed (chapter 5); and their concentrations in ambient air (chapter 6). Volume III contains the documentation of the effects of photochemical oxidants on vegetation, ecosystems, and nonbiological materials. Volume IV contains the extensive body of data available on the toxicological effects of ozone and other oxidants in experimental animals and on *in vitro* effects on human cells and body fluids. In Volume V, effects observed in human controlled exposures (chapter 11) and in epidemiological studies (chapter 12) are presented. In addition, that volume contains an evaluation of the integrated health data of probable consequence for regulatory purposes (chapter 13).

It must be emphasized that neither control techniques nor control strategies for the abatement of photochemical oxidants are discussed in this document. Technology for controlling the emissions of nitrogen oxides and of volatile organic compounds is discussed in documents issued by the Office of Air Quality Planning and Standards (OAQPS). Likewise, issues germane to the scientific basis for control strategies, but not germane to the development of criteria, are addressed in respective documents issued by OAQPS.

In addition, certain issues of direct relevance to standard-setting are not explicitly addressed in this document: (1) determination of what constitutes an "adverse effect"; (2) assessment of risk; and (3) determination of a margin of safety. While scientific data contribute significantly to decisions regarding these issues, their resolution cannot be achieved solely on the basis of experimentally acquired information. A fourth issue directly pertinent to standard-setting is addressed partially in chapter 13 of this document; that is, identification of the population at risk. The selection of the population at risk is basically a selection by the Agency of the population to be protected by the promulgation of a given standard. Information is presented in chapter 13 of this document on factors, including pre-existing disease, that biologically may predispose individuals and subpopulations to adverse effects from exposures to ozone. The identification of a population at risk, however, requires information above and beyond biological predisposition, such as levels of exposure, activity patterns, and personal habits. Thus, the identification of the population at risk relative to standard-setting is the purview of OAQPS and is not fully addressed in this document.

This document contains a review and evaluation of literature on ozone and other photochemical oxidants through early 1984. Emphasis has been placed on studies in which concentrations were similar to those found in the ambient air. On this basis, studies in which the lowest concentration employed exceeded 1 ppm have not been included unless the report contained unique data, such as documentation of a previously unreported effect or of mechanisms of effects. The one exception is in the areas of mutagenesis, teratogenesis, and reproductive effects, where, because of their importance to public health and welfare, results of studies conducted at much higher than ambient levels have been included.

A general policy exists within EPA of expressing concentrations of gas-phase criteria pollutants in micrograms per cubic meter ($\mu g/m^3$) as well as the more widely used parts per million (ppm) or parts per billion (ppb). That policy has been followed in those chapters in which the bulk of the data have been obtained from laboratory studies done at room temperature (e.g., chapters 10 and 11). Data reported in ppm for studies done out of doors, such as field and open-top chamber vegetation studies, ambient air monitoring, and research on atmospheric chemistry, have not been converted. Conversion of reported ppm and ppb units is highly questionable in these cases because it assumes standard or uniform temperatures and pressures. For data in the health chapters, the conversion units used are 1 ppm ozone = 1960 $\mu g/m^3$; 1 ppb PAN = 4947 $\mu g/m^3$; at 1 atmosphere pressure and 25°C.

2.4 REFERENCES

U.S. Congress. (1977) The Clean Air Act as amended August 1977. P.L. 95-95. Washington, DC: U.S. Government Printing Office.

U.S. Environmental Protection Agency. (1978) Air quality criteria for ozone and other photochemical oxidants. Research Triangle Park, NC: U.S. Environmental Protection Agency; EPA report no. EPA-600/8-78-004.

U.S. Environmental Protection Agency. (1982a) Air quality criteria for oxides of nitrogen. Research Triangle Park, NC: U.S. Environmental Protection Agency; EPA report no. EPA-600/8-82-026.

U.S. Environmental Protection Agency. (1982b) Air quality criteria for particulate matter and sulfur oxides. Research Triangle Park, NC: U.S. Environmental Protection Agency; EPA report no. EPA-600/8-82-029.

3. PRECURSORS TO OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

3.1 INTRODUCTION

Ozone and other photochemical oxidants are almost exclusively secondary pollutants that are formed in the troposphere from primary pollutants emitted into the ambient air from a variety of sources. Ozone-rich stratospheric air and lightning constitute the only direct sources of ozone that are known to contribute to the ambient air concentrations of ozone. Their contributions are variable and minor. The primary pollutants that serve as precursors to the formation of ozone and other photochemical oxidants are volatile nonmethane organic compounds (NMOC) and nitrogen oxides (NO_x).

The purpose of this chapter is to present to the reader an overview of the chemistry, measurement, sources, abundance, and transformation of precursors in the United States in order (1) to convey an understanding of the oxidant problem; (2) to convey an appreciation for the complexities of the production and, hence, the abatement of oxidant pollution; and (3) to convey information on the current status of and any anticipated changes in the kind, magnitude, and distribution of precursors to oxidant formation.

3.2 DESCRIPTION AND CHARACTERIZATION OF PRECURSORS

3.2.1 Description and Basic Nomenclature of Nonmethane Organic Compounds

This section briefly describes and defines those hydrocarbons and other volatile organic compounds commonly found in the ambient air in urban and rural areas of the United States.

The term "hydrocarbon" has been used since the preliminary investigations of tropospheric photochemistry to represent those compounds of carbon and hydrogen that exist as gases in the ambient air and that participate along with oxides of nitrogen in reactions that form ozone and other photochemical oxidants. As knowledge of photochemistry has increased, carbon compounds containing elements such as oxygen and the halogens have been discovered to be important also in the formation of the urban photochemical complex. Thus, the term "volatile organic compounds" (VOC) has come to be used to describe stable organic compounds that exist as gases under normal atmospheric conditions and that participate in the formation of photochemical oxidants. Recognition that methane (CH_4) is virtually unreactive in the photochemical formation of ozone and other oxidants has given rise to an even more accurate term, "nonmethane organic compounds" (NMOC), for describing those gas-phase organic compounds in ambient air that serve as precursors to ozone and other photochemical oxidants. While these three terms may sometimes appear to be used interchangeably in this chapter, the terminology used reflects the terminology reported in the specific literature cited in this chapter, though in some instances differentiations may have been made for purposes of discussion.

As discussed in Section 3.3 below, methods for measuring gas-phase hydrocarbons are not specific for hydrocarbons but may also detect other gas-phase organic compounds, though they will not measure them accurately. Where methods are used that permit speciation of the compounds measured, organic compounds other than hydrocarbons can be and usually are excluded from the summation of individual species used to arrive at a total nonmethane hydrocarbon (TNMHC) concentration. Where researchers have used methods that do not permit speciation, an indefinite and variable fraction of the reported TNMHC concentration may, in fact, be the result of the presence of nonhydrocarbon organics and such concentration data are more properly reported as total nonmethane organic compounds (NMOC).

The discussion that follows is aimed at presenting basic facts on nomenclature and characteristics of photochemically reactive volatile organic compounds that are relevant to the information given in subsequent sections of this chapter and in the subsequent chapter.

3.2.1.1 Hydrocarbons. Hydrocarbons are compounds consisting of hydrogen and carbon only. Except for carbides, carbonates, and oxides of carbon, all compounds of carbon are organic. The volatility of hydrocarbons is related generally to the number of carbon atoms in each molecule, as well as to temperature. Hydrocarbons with a carbon number of one to four are gaseous at ordinary temperatures, while those with a carbon number of five or more are liquid or solid in pure state. Liquid mixtures of hydrocarbons such as gasoline may include some compounds that are gases, as well as those that are liquids, in pure form. Likewise, gas-phase mixtures in ambient air will usually include compounds that are liquid in their pure form. Hydrocarbons with a carbon number of about 8 or less are abundant in ambient air, but those with a carbon number greater than about 12 are generally not present at gaseous concentrations high enough to be troublesome. A saturated hydrocarbon has each of its carbon atoms bonded to four other atoms; whereas an unsaturated hydrocarbon has two or more carbon atoms bonded to fewer than four other atoms.

Alkanes. Alkanes, also known as paraffins, are saturated hydrocarbons having the general formula C_nH_{2n+2}. The first compound in the series is methane, CH_4, which is unimportant in urban photochemistry because of its low reactivity. Alkanes as a class are the least reactive of the photochemically important hydrocarbons (U.S. Environmental Protection Agency, 1978). Alkanes may be straight- or branched-chain compounds, and are a subclass of the open-chain (acyclic) hydrocarbons known as aliphatic hydrocarbons.

Alkenes. Alkenes, also known as olefins, have at least one unsaturated bond. The number of hydrogen atoms in the general formula is decreased by two for each double bond between carbon atoms, and the general formula for alkenes with one double bond is C_nH_{2n}. The first compound in the alkene class is ethene, also known as ethylene; the second is propene, also known as propylene. Compounds with carbon numbers three or higher can have two double bonds between carbons and are called dienes. The complete name of a diene is formed by including a prefix with numbers that indicate the location of the double bonds. Like alkanes, alkenes are aliphatic hydrocarbons and may exist as straight or branched chains. As a class, alkenes are the most reactive hydrocarbons in photochemical systems. The reader is referred to the brief discussion on reactivity in section 3.2.2 and to discussions in Pitts et al. (1977) and Dimitriades (1974).

Terpenes. Terpenes are a naturally occurring subgroup of alkenes having the formula $C_{10}H_{16}$. Among the terpenes identified in ambient air, α- and β-pinene have been most frequently studied. Both α- and β-pinene contain six-membered rings, do several other terpenes; but at least one commonly occurring member of this group, myrcene, is an acyclic or open-chain compound. Isoprene, also an olefinic hydrocarbon that is naturally occurring, is a hemiterpene having the formula C_5H_8.

Alkynes. Alkynes are open-chain hydrocarbons that contain one or more triple bonds. Acetylene, C_2H_2, is the simplest member of the class and the class as a whole is often referred to as the acetylenes. The general formula for the acetylenes is C_nH_{2n-2}, and for each additional triple bond in the molecule four hydrogen atoms must be removed from the general formula. Acetylene is commonly present in ambient air, is thought to be emitted largely from mobile sources, and has often been measured as an indicator of auto exhaust emissions, since it is relatively unreactive in ambient air and persists in the atmosphere longer than most other exhaust components.

Alicyclics. Alicyclics are hydrocarbons in which the carbon chains are arranged in rings (carbocyclic). They can be saturated compounds containing no double bonds or may be unsaturated compounds containing one to three double bonds. They may contain six-membered rings, but they do not possess the six-membered ring containing three double bonds in resonance that is characteristic of aromatic hydrocarbons. The carbocyclic group may have alkyl substituents or may be attached to more complex groups, including aliphatic chains. The conventions of nomenclature applied to aliphatic compounds generally apply also to alicyclics.

Aromatics. Aromatic hydrocarbons include various compounds having atoms arranged in six-membered carbon rings with only one additional atom (of hydrogen or carbon) attached to each atom in the ring. Benzene is the simplest compound in the series, having no side chains but only six carbon atoms and six hydrogen atoms, linked by three conjugated double bonds.

Compounds containing the aromatic ring and elements other than carbon and hydrogen are included with aromatic hydrocarbons in the general classification "aromatics." The double bonds in aromatics are not nearly as chemically active as those in alkenes because of an effect called "resonance stabilization." As a class, aromatics are between alkanes and alkenes in photochemical reactivity. Benzene, however, is considered to have low photochemical reactivity.

3.2.1.2 Aldehydes. Aldehydes are not true hydrocarbons, since they always contain at least one oxygen atom. Nevertheless, they constitute probably the single most abundant group of volatile organic compounds other than hydrocarbons in the ambient air. They are photochemically important compounds because, along with other oxidizable compounds such as the hydrocarbons, they regenerate free radicals that will react with oxygen in ambient air to form alkylperoxy or hydroperoxy radicals (National Academy of Sciences, 1977) (see chapter 4).

Aldehydes are characterized by the presence of the formyl functional group (CHO). As part of the formyl group, a carbonyl group exists, C=O, having a carbon-oxygen double bond. The carbonyl group is not unique to aldehydes, since it is found also in ketones and carboxylic acids, as well as in more complex organic molecules such as the sugars. The carbonyl group forms the basis, however, for one of the analytical methods used for measuring aldehydes in ambient air (section 3.3).

3.2.1.3 Other Organic Compounds. Other organic compounds found in ambient air are known to be photochemically reactive in the formation of ozone and other photochemical oxidants. These other organic compounds do not occur in ambient air collectively, much less singly, at concentrations that even approach the concentrations of nonmethane hydrocarbons. Some of them are suspected of having adverse health effects, however, and are therefore under scrutiny by the U.S. Environmental Protection Agency at present, and documents dealing with such compounds are in preparation by the Agency. These compounds are mentioned here only because they are photochemically reactive, can serve as precursors to oxidants, and because they contribute a small but indeterminate fraction of the total NMOC concentrations reported when continuous hydrocarbon analyzers (section 3.3) are used to determine the occurrence in ambient air of volatile organic compounds.

Many of the volatile organics in ambient air that are not hydrocarbons are organic halides, in which one or more hydrogen atoms of a hydrocarbon have been replaced by a halogen such as chlorine, fluorine, or iodine. When all the hydrogen is replaced, the resulting compounds are called halocarbons. An enormous number of relatively simple organic halides are possible, since a single carbon atom can be attached to one or more halogen atoms.

A number of halogenated hydrocarbons enjoy widespread industrial use as commercial solvents for extraction and reaction media and for direct application as cleaning and degreasing solvents. Many of these have been detected in ambient air.

3.2.2 Pertinent Chemical and Physical Properties of Nonmethane Organic Compounds

The chemical and physical properties of nonmethane organic compounds that are most pertinent to their role as precursors to ozone and other oxidants are those properties that govern their emission into and persistence in the atmosphere (volatility) and their reactivity in atmospheric photochemical reactions. A major discussion of these properties lies outside the scope of this document, inasmuch as such a discussion would necessitate a much more thorough review of atmospheric photochemistry than is relevant to the purposes of this document. The photochemical reactivity of subclasses and individual species of hydrocarbons and of other volatile organic compounds is relevant to mechanistic studies in atmospheric chemistry and to modeling and other oxidant-control-related research but is not pertinent to the derivation of criteria. By way of illustration, however, of the differences in reactivity, some very general comments are in order.

The 1978 criteria document for ozone and other photochemical oxidants summarized reactivity data acquired from the mid-1960s to the mid-1970s (U.S. Environmental Protection Agency, 1978). Reference to tables of reactivity schemes given in the 1978 document shows the relatively higher reactivities of internally double-bonded alkenes, of aliphatic aldehydes and other carbonyl compounds (such as branched alkylketones and unsaturated ketones), of dienes, of 1-alkenes, of partially halogenated alkenes, and of alkylbenzenes (primary and secondary monoalkylbenzenes, and di-, tri-, and tetraalkylbenzenes). Other compounds also have relatively high reactivity but are not expected to be as abundant in ambient air as the compounds cited above. The reader is referred to the 1978 criteria document and the references therein for further information on reactivities of specific compounds. The concentrations at which respective classes and species of NMOC occur in ambient air are presented in section 3.5.

The chief basis of most of the proposed reactivity classifications is the rate of reaction between an organic and the hydroxyl radical (HO· or OH·). A key reaction of volatile organic compounds in ambient air, regardless of class of VOC, is their oxidation via attack by HO· (Atkinson et al., 1979; Atkinson et al., 1982). This reaction is the first step in a chain reaction that is propagated by various organic peroxy radicals. It is thought to be the predominant loss process for most organics in the troposphere (Atkinson et al., 1982), even for alkanes, for which rate constants for their reactions with HO· are lower than the alkenes of equivalent carbon numbers (Atkinson et al., 1979).

Alkenes are unique among VOC in ambient air, inasmuch as they exhibit reactivity toward ozone as well as toward the hydroxyl radical (Niki et al., 1983). In addition, the reactions of alkenes subsequent to the initial reaction with HO· are much better understood for the alkenes than for alkanes or aromatics. The reaction scheme accepted at present for the HO·-initiated oxidation of trans-2-butene, as an example of the alkenes, is given in chapter 4 in some detail.

Subsequent reactions, following HO· attack, are complex for the longer-chain alkanes and are at present rather poorly understood for haloalkanes, haloalkenes, and for aromatics, including the halogenated aromatics. For all of these compounds, as well as for oxygenated organics, the initial step is attack by the hydroxyl radical. Whether the next step is hydrogen abstraction, addition of OH to a double bond, or the formation of an energy-rich OH-organic adduct depends largely upon the structure of the organic, although temperature and pressure dependencies have been observed in experimental smog chamber work (Atkinson et al., 1979; 1980). In fairly recent work, Killus and Whitten (1982) proposed that ring opening can occur in toluene (an aromatic) subsequent to the formation of an OH-toluene adduct, resulting in products unlike those occurring from HO· attack on alkanes or alkenes.

Reactivities in ambient air are not necessarily the same as in smog chamber systems. For example, source strength, meteorological variables, transport, and the age of the air mass containing the VOC are all known to affect reactivity. The discussion above, however, presents some of the basic generalizations that are pertinent to the photochemical reactivity of various classes of VOC in ambient air.

3.2.3 Description and Properties of Nitrogen Oxides

The physical and chemical properties of the nitrogen oxides that serve as precursors in the formation of ozone and other photochemical oxidants have been documented in a recent air quality criteria document (U.S. Environmental Protection Agency, 1982). The most pertinent properties are briefly summarized here. The role of nitrogen oxides in the formation of oxidants in the troposphere is discussed in chapter 4 and in the document cited above.

The three most abundant oxides of nitrogen in ambient air are nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O). The latter, though ubiquitous, is not known to participate in photochemical reactions in the troposphere. The two important oxides of nitrogen relative to photochemical processes in the troposphere are NO and NO_2. Their importance derives from their abundance in ambient air and their participation in cyclic reactions leading to the production of ozone and other oxidants, as described in chapter 4. The basic reactions of importance are (1) the photolysis of NO_2 ($\lambda < 430$ nm);

(2) subsequent formation of ozone (O_3) from the atomic oxygen produced in the photolysis of NO_2 (in the presence of a third, energy-absorbing molecule); and (3) the subsequent regeneration of NO_2 by the reaction of NO with O_3. Coupled with these basic reactions are reactions between NO and free radicals in the atmosphere (hydroperoxy, alkylperoxy, and acylperoxy) that oxidize NO to NO_2, disturbing the NO-NO_2 equilibrium that would otherwise exist, and leading, then, to the buildup of O_3 (National Academy of Sciences, 1977). These reactions, and further information on the source of the free radicals, are given in chapter 4. Basic physical and chemical properties of NO and NO_2 are given in Table 3-1.

TABLE 3-1. PHYSICAL AND CHEMICAL PROPERTIES
OF NITRIC OXIDE AND NITROGEN DIOXIDE

Property	NO	NO_2
Odor	None	Pungent
Taste	-	-
Color	None	Reddish-brown
Absorption λ, nm[a]	<230	Broad range, both >400 and <400
Other properties of note:		Corrosive, strong oxidant. Photolyzes at λ <430 nm. Low partial pressure in ambient air. Uneven number of valence electrons. Forms dimers (N_2O_4).

[a] Visible light λ >400 nm; ultraviolet λ <400 nm. Solar UV radiation in the troposphere extends from about λ230 nm to about λ400 nm.

Source: Derived from National Academy of Sciences (1977) and U.S. Environmental Protection Agency (1982).

3.3 SAMPLING, MEASUREMENT, AND CALIBRATION METHODS FOR PRECURSORS TO OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

During the last decade, a number of advances have been made in the methodology for determining nonmethane organic compounds (NMOC) and oxides of nitrogen. An overview of these advances will be discussed in this chapter. In the case of NMOCs, early methods did not provide for any speciation of the complex mixture of organics in ambient air. Nonetheless, these non-speciation methods were employed and served a useful purpose in providing a data base for early photochemical modeling studies. As the air quality models grew more sophisticated, however, the need arose for more specific information concerning the organic composition of the atmosphere. Consequently, methodology was developed to provide for detailed speciation of NMOCs. In addition to improving the data base for photochemical modeling, the NMOC speciation techniques have also been utilized to characterize various sources of pollution (mobile versus stationary) and have led to the identification and quantification of many compounds not previously identified in the ambient air.

The development of methodology for oxides of nitrogen has likewise advanced since the original EPA Federal Reference Method for measurement of nitrogen dioxide (NO_2), the Jacobs-Hochheiser technique, was withdrawn in 1973. A number of methods for nitric oxide (NO) and NO_2 have been proposed and evaluated since then. Information on these more recent methods is presented in this section.

3.3.1 Nonmethane Organic Compounds

Numerous sampling, measurement, and calibration methods have been employed to determine vapor-phase nonmethane organic compounds (NMOC) in ambient air. Some of the measurement methods utilize detection techniques that are highly selective and sensitive to specific functional groups or atoms of a compound (e.g., formyl group of aldehydes, halogen), while others respond in a more universal manner; that is, to the number of carbon atoms present in the organic molecule. In order to present an overview of the most pertinent measurement methods, nonmethane organic compounds have been arranged in three major classifications in this section. These classifications are "nonmethane hydrocarbons," "aldehydes," and "other oxygenated compounds." Each classification and the associated measurement methods will be discussed. Sampling and calibration procedures used with these measurement methods will also be described. Reference will also be made to those analytical methods utilized in more than one of the above classifications.

3.3.1.1 Nonmethane Hydrocarbons. Nonmethane hydrocarbons constitute the major portion of nonmethane organic compounds in ambient air (section 3.5). Traditionally, nonmethane hydrocarbons have been measured by methods that employ a flame ionization detector (FID) as the sensing element. This detector was originally developed for gas chromatography and employs a sensitive electrometer that measures a change in ion intensity resulting from the combustion of air containing organic compounds. Ion formation has been shown to be essentially proportional to the number of carbon atoms present in the organic molecule (Sevcik, 1975). Thus, aliphatic, aromatic, alkenic, and acetylenic compounds all respond similarly to give relative responses of 1.00 ± 0.10 when corrected for the number of carbon atoms present (e.g., 1 ppm hexane = 6 ppm C; 1 ppm benzene = 6 ppm C; 1 ppm propane = 3 ppm C). Carbon atoms bound to oxygen, nitrogen, or halogens give reduced relative responses (Dietz, 1967). Consequently, the FID, which is primarily used as a hydrocarbon measuring method, should more correctly be viewed as an organic carbon analyzer.

In the following sections, discussion will focus on the various methods utilizing this detector to measure nonmethane organics. Those methods for total nonmethane organic compounds in which no compound speciation is obtained will be covered first. Methods for determining individual compounds will then be discussed.

3.3.1.1.1 Non-speciation methods. The EPA reference method for nonmethane organic compounds, which was promulgated in 1971, involves the gas chromatographic separation of methane (CH_4) from the remaining organics in an air sample (U.S. Environmental Protection Agency, 1975). Methane is eluted through the chromatographic column and detected; another sample of air is subsequently processed without methane separation. Subtraction of the first value from the second produces a nonmethane organic concentration.

A number of studies of commercial analyzers employing the Federal Reference Method have been reported (Reckner, 1974; McElroy and Thompson, 1975; Harrison et al., 1977; Sexton et al., 1981). In one of the first studies, the analyses of known synthetic mixtures of hydrocarbons were conducted by 16 users of the reference method (Reckner, 1974). The nonmethane concentrations tested in this study were 0.23 and 2.90 ppm C. The results shown in Table 3-2 indicate the percentage error from the two known concentrations. At the 0.23 ppm level, the majority of the measurements were in error by amounts greater than 50 percent. At 2.90 ppm, most of the measurements were in error by only 20 percent or less.

In general, all of the above studies indicated an overall poor performance of the commercial instruments when either calibration or ambient mixtures containing NMOC concentrations less than 1 ppm C were used. The major problems

TABLE 3-2. PERCENTAGE DIFFERENCE FROM KNOWN CONCENTRATIONS OF NONMETHANE HYDROCARBONS OBTAINED BY SIXTEEN USERS

Known concentration, ppm	% difference from given concentration				
	>100	50 to 100	20 to 50	10 to 20	0 to 10
0.23	6	4	3	2	1
2.90	2	--	3	2	9

Source: Reckner, 1974.

associated with these instruments have been summarized in a recent technical assistance document (U.S. Environmental Protection Agency, 1981) for the calibration and operation of ambient-air nonmethane organic compound analyzers. Table 3-3 lists these shortcomings. The first three problems have essentially been corrected through work done at the National Bureau of Standards. The assistance document further summarizes ways to reduce the effects of existing problems and Table 3-4 presents these recommendations.

As a result of the above deficiencies, other approaches to the measurement of nonmethane organics have been investigated. One such method, developed in 1973, utilizes the fact that CH_4 requires more heat for combustion than other organics (Poli and Zinn, 1973). One portion of the air sample passes through a catalyst bed where all hydrocarbons except CH_4 are combusted. This sample stream then enters an FID where the CH_4 concentration alone is recorded. The other portion of the sample passes directly to a second FID for a total organic carbon measurement. By simultaneously processing both signals, an NMOC value is obtained. Although it provides a continuous measurement of NMOC levels, this method is also subject to many of the same shortcomings attributed to the EPA reference method.

Recently, a prototype instrument that measures NMOCs by optical absorption has been developed (Manos et al., 1982). The unit oxidizes NMOCs to carbon dioxide (CO_2) and uses a non-dispersive infrared absorption technique to measure the organic burden indirectly. Ascarite serves to remove CO_2 initially present in air and a hopcalite catalyst selectively oxidizes organics other than methane to CO_2 and H_2O. Since carbon monoxide (CO) will also oxidize to CO_2 during this process, a dual-channel system is utilized to correct for the

TABLE 3-3. SUMMARY OF PROBLEMS ASSOCIATED WITH GATHERING NMOC DATA BY MEANS OF AUTOMATED ANALYZERS

1. Contaminants may be present in compressed-gas cylinders containing calibration gases.
2. Compressed-gas cylinders of calibration gases sometimes contain the standard in a nitrogen or argon background. When no oxygen is blended with these gases, FID sensitivity is altered.
3. The assay of calibration gases contained in compressed-gas cylinders (as received from the supplier) is sometimes incorrect.
4. There are wide differences in the per-carbon response to different NMOC species.
5. FID analyzers require hydrogen, which presents a potential operational hazard.
6. The NMOC concentration is obtained by subtraction of two relatively large and nearly equal numbers ($TOC-CH_4=NMOC$) and thus is subject to large, relative errors.
7. NMOC analyzers may exhibit excessive zero and span drift during unattended operation.
8. The complex design of some NMOC analyzers creates unique problems that are generally not experienced in other pollutant analyzers. Meticulous set-up, calibration, and operation procedures (which are analyzer-specific) are difficult to understand and follow.

Source: U.S. Environmental Protection Agency, 1981.

contribution from ambient CO concentrations. This unit performed well during a brief laboratory evaluation using calibration standards; however, more extensive laboratory and field tests are needed before the unit can be considered suitable for NMOC measurement.

Other methods under development and evaluation include oxidation-reduction schemes in which nonmethane organics are chromatographically separated from methane and non-organic species and then oxidized to CO_2, reduced to CH_4, and detected by FID (U.S. Environmental Protection Agency, 1979). In cases where organic carbon concentrations are greater than 100 ppb, the reduction step in this method can be eliminated and a non-dispersive infrared analyzer can be used to detect the CO_2 formed during the oxidation step (Salo et al., 1975).

TABLE 3-4. SUMMARY OF RECOMMENDATIONS TO REDUCE THE EFFECTS OF PROBLEMS LISTED IN TABLE 3-3

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1. Calibration gases should be checked to determine the concentration of contaminants.
2. Calibration concentrations should be obtained by dynamic dilution of a pollutant standard with zero-grade air containing oxygen. The dilution ratio should be sufficiently high (~100:1) to ensure that the calibration sample contains 20.9% ± 0.3% oxygen.
3. All calibration standards contained in compressed-gas cylinders should be traceable to Standard Reference Materials from the National Bureau of Standards.
4. The NMOC response should be calibrated to a propane standard.
5. The operator should use documented procedures for hydrogen safety.
6. All channels should be properly calibrated.
7. The FIDs should be operated in accordance with instructions supplied by the manufacturer and this document.
8. The training of qualified operators should be augmented with a Technical Assistance Document, which provides detailed calibration and operation procedures for NMOC analyzers.

Source: U.S. Environmental Protection Agency, 1981.

A unique total NMOC measurement technique has resulted from the initial work of McBride and McClenny (1980). Their approach involved the cryogenic preconcentration of nonmethane organic compounds and the measurement of the revolatilized NMOCs using flame ionization detection. Their procedure is as follows. A fixed volume of sample is drawn through a trap cooled to liquid argon temperature (liquid N_2 can not be used since it will also condense methane and air). At this temperature all NMOCs are condensed onto the trap (open tube). After the residual CH_4 and oxygen are cleared from the trap by the helium carrier gas, the trap temperature is raised to revolatilize the NMOC. Using helium as the carrier gas was shown to produce less variation in response to different organic compounds than direct air injection, which is employed in conventional NMOC analyzers.

Jayanty et al. (1982) improved upon the original design of McBride and McClenny (1980) and evaluated the resulting system with a variety of aliphatic and aromatic compounds. The range of detection with the cryogenic trapping procedure (500 ml of air) was about 50 ppb C and a linear dynamic range of 50 to 5,000 ppb C was attained. Humidity did not generally interfere with the analysis. Sample precisions of ±5 percent for single- and multiple-component gas standards and ±10 percent for ambient samples were consistently achieved. Responses for aromatic compounds, however, were less than expected. The researchers recommended additional testing and instrument refinement in order to resolve this problem.

3.3.1.1.2 Speciation methods. The primary separation technique utilized for NMOC speciation is gas chromatography (GC). Coupled with flame ionization detection, this analytical method permits the separation and identification of many of the organic species present in ambient air.

Compound separation is accomplished by means of both packed and capillary GC columns. If high resolution is not required and large sample volumes are to be injected, packed columns are employed. The traditional packed column may contain either (1) a solid polymeric adsorbent (gas-solid chromatography) or (2) an inert support, coated with a liquid (gas-liquid chromatography). Packed columns containing an adsorbent substrate are required to separate C_2-C_3 compounds. The second type of column can be a support-coated or wall-coated open tubular capillary column. The latter column has been widely used for environmental analysis because of its superior resolution and broader applicability. The wall-coated capillary column consists of a liquid stationary phase coated or bonded (cross-linked) to the specially treated glass or fused-silica tubing. Fused-silica tubing is most commonly used because of its physical durability and flexibility.

When a complex mixture is introduced into a GC column, the carrier gas (mobile phase) moves the sample through the packed or coated column (stationary phase). The chromatographic process occurs as a result of repeated sorption-desorption of the sample components (solute) as they move along the stationary phase. Separation results from the different affinities that the solute components have for the stationary phase.

The GC-FID technique has been used by numerous researchers to obtain ambient NMOC data (see section 3.4). In a recent report, Singh (1980) utilized the cumulative experience of these researchers in order to prepare a guidance document for the state and local air pollution agencies interested in obtaining speciation data. In general, most researchers have employed two gas chromatographic units to carry out analyses of NMOC species in ambient air. Organic compounds of C_2 through C_5 are easily measured on one unit using packed-column technology, while the other GC separates $\geq C_4$ organics using a capillary column. Figures 3-1 and 3-2 and Table 3-5 illustrate typical chromatograms of NMOCs found in urban air. As these figures indicate, all the major peaks eluted have been identified; on a mass basis, these compounds represent from 65 to 90 percent of the measurable nonmethane organic burden. Identification of GC peaks is based upon matching retention times of unknowns with those of standard mixtures. The use of dedicated computer systems facilitates this task, but close scrutiny of the data is still necessary in order to correct periodic mis-identification of unknowns resulting from variations in retention time. Subsequent verification of the individual species is normally accomplished with gas chromatographic/mass spectrometric (GC/MS) techniques. Compound-specific detection systems, such as electron capture, flame photometry, and spectroscopic techniques, have also been employed for peak identifications. A discussion of these systems, however, is beyond the scope of this report. Several documents covering these detection systems are available (Lamb et al., 1980; Riggin, 1983).

Because the organic components of the ambient atmosphere are present at ppb levels or lower, some means of sample preconcentration is necessary in order to provide sufficient material for the GC-FID system. The two primary techniques utilized for this purpose are cryogenic collection and the use of solid adsorbents. The more commonly used sorbent materials are generally divided into three categories: (1) organic polymeric adsorbents, (2) inorganic adsorbents, and (3) carbon adsorbents. Primary organic polymeric adsorbents used for NMOC analyses include the materials Tenax GC and XAD-2. These materials have a low retention of water vapor and, hence, large volumes of air can be collected. These materials do not, however, efficiently capture highly volatile compounds such as C_2 to C_5 hydrocarbons, nor certain polar compounds such as methanol and acetone. Primary inorganic adsorbents are silica gel, alumina, and molecular sieves. These materials are more polar than the organic polymeric adsorbents and are thus more efficient for the collection of the more volatile and polar compounds. Unfortunately, water is also efficiently collected, which in many instances leads to rapid deactivation of the adsorbent. Carbon adsorbents are less polar than the inorganic adsorbents and, as a result, water adsorption by carbon adsorbents is a less significant problem. The

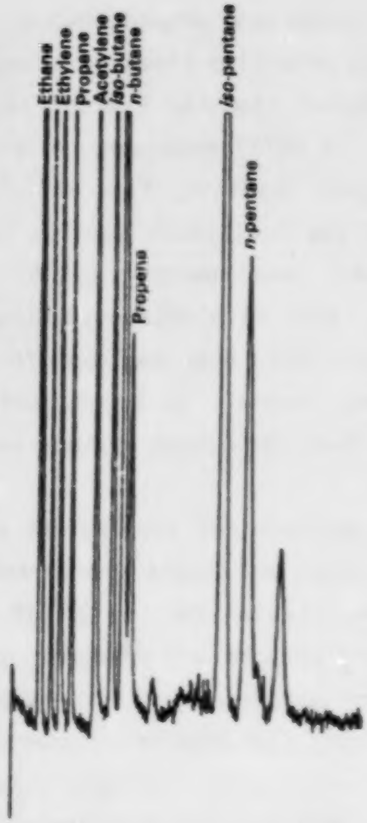

Figure 3-1. Light hydrocarbon chromatogram (C_2 to C_6) from the university campus site, Cincinnati, Ohio, August 24, 1981.

Source: Holdren et al. (1982).

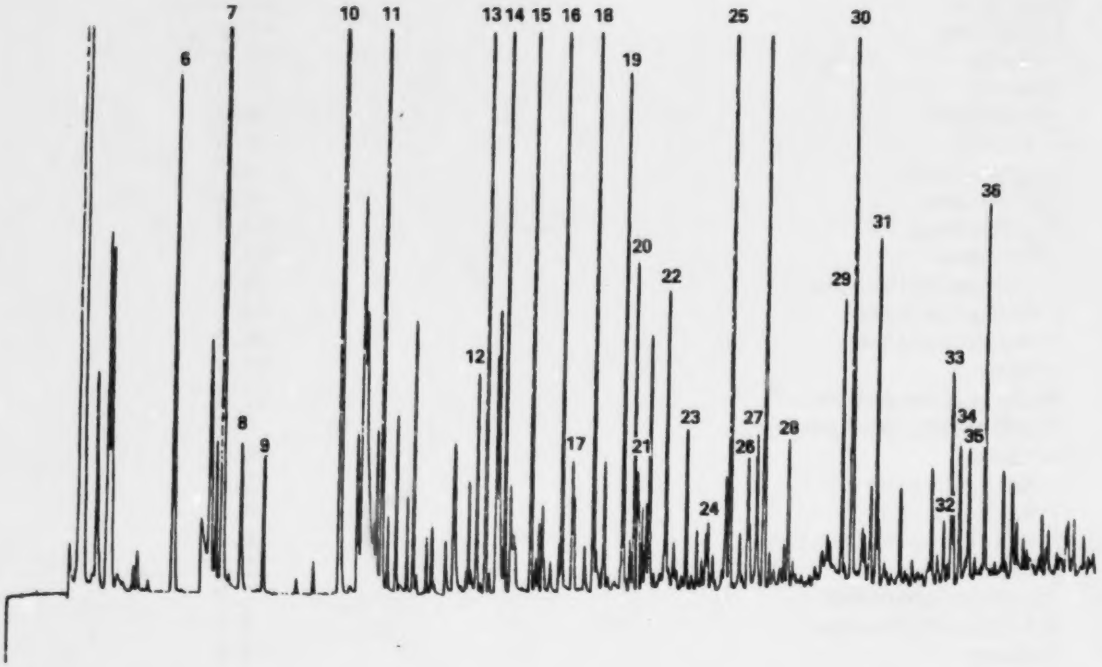

Figure 3-2. Heavy hydrocarbon chromatogram (C_4 to C_{10}) from university campus site, Cincinnati, Ohio, August 24, 1981.

Source: Holdren et al. (1982).

TABLE 3-5. IDENTIFICATION KEY FOR TYPICAL HEAVY HYDROCARBON CHROMATOGRAM, C_4 TO C_{10} (UNIVERSITY CAMPUS SITE, CINCINNATI, OHIO, AUGUST 24, 1981)

	Hydrocarbon	Concentration, ppb C
1.	Ethane	43.2
2.	Ethylene	113.5
3.	Acetylene	44.1
4.	Propane	28.8
5.	Propene	29.8
6.	iso-Butane	44.3
7.	n-Butane	115.9
8.	trans-Butene	9.7
9.	cis-Butene	6.4
10.	iso-Pentane	137.3
11.	n-Pentane	68.6
12.	2,3-Dimethylbutane	11.1
13.	2-Methylpentane	42.8
14.	3-Methylpentane	28.0
15.	n-Hexane	33.7
16.	Methylcyclopentane	27.2
17.	2,4-Dimethylpentane	4.2
18.	Benzene	35.1
19.	2-Methylhexane	25.6
20.	3-Methylhexane	14.6
21.	2,2,4-Trimethylpentane	5.2
22.	n-Heptane	15.1
23.	Ethylcyclopentane	7.7
24.	2,4-Dimethylhexane	3.1
25.	Toluene	73.5
26.	2-Methylheptane	6.7
27.	3-Methylheptane	9.2
28.	n-Octane	6.9
29.	Ethylbenzene	12.5
30.	m- + p-Xylene	42.4
31.	o-Xylene	15.3
32.	n-Propylbenzene	3.6
33.	p-Ethyltoluene	9.5
34.	1,3,5-Trimethylbenzene	7.8
35.	o-Ethyltoluene	7.9
36.	1,2,4-Trimethylbenzene	17.2
	Identified NMOC	1108
	Unidentified NMOC	762
	Total NMOC	1870

Source: Holdren et al., 1982.

carbon-based materials also tend to exhibit much stronger adsorption properties than organic polymeric adsorbents; thus, lighter-molecular-weight species are more easily retained. These same adsorption effects result, however, in irreversible adsorption of many compounds. Furthermore, the very high thermal desorption temperatures required (350 to 400 °C) limit their use and also may lead to degradation of labile compounds. The commonly available classes of carbon adsorbents include: (1) various conventional activated carbons; (2) carbon molecular sieves (Spherocarb, Carbosphere, Carbosieve); and (3) carbonaceous polymeric adsorbents (Ambersorb XE-340, XE-347, XE-348).

Although a number of researchers have employed solid adsorbents for the characterization of selected organic species in air, only a few attempts have been made to identify and quantitate the range of organic compounds from C_2 and above. Westberg et al. (1980) evaluated several carbon and organic polymeric adsorbents and found that Tenax-GC exhibited good collection and recovery efficiencies for $\geq C_6$ organics; the remaining adsorbents tested (XAD-4, XE-340) were found unacceptable for the lighter organic fraction. The XAD-4 retained $\geq C_2$ organic gases, but it was impossible to completely desorb these species without partially decomposing the XAD-4. Good collection and recovery efficiencies were provided by XE-340 only for organics of C_4 and above.

Ogle et al. (1982) used a combination of adsorbents in series and designed an automated GC-FID system for analyzing C_2 through C_{10} hydrocarbons. Tenax GC was utilized for C_6 and above, while Carbosieve S trapped C_3 through C_5 organics. Silica gel followed these adsorbents and effectively removed water vapor while passing the C_2 hydrocarbons onto a molecular-sieve 5A adsorbent. The combined sorbents have been laboratory-tested with a 38-component hydrocarbon mixture. Good collection and recovery efficiencies were obtained. Preliminary field tests have also been successful, but a very limited data base exists. Futhermore, the current chromatographic procedures utilize packed-column technology. The addition of capillary columns to this system would permit better resolution of the complex mixtures typically found in ambient air.

Presently, the preferred method for obtaining NMOC data is cryogenic preconcentration (Singh, 1980). Sample preconcentration is accomplished by directing air through a packed trap immersed in either liquid oxygen (b.p. -183°C) or liquid argon (b.p. -186°C). For the detection of about 1 ppb C of an individual compound, a 250-cc air sample is normally processed. The collection trap is generally filled with deactivated 60/80 mesh glass beads (Westberg et al., 1974), although coated chromatographic supports have also been used (Lonneman et al., 1974). Both of the above cryogens are sufficiently warm to allow air to pass completely through the trap, yet cold enough to collect trace organics efficiently. This procedure will also condense water vapor. An air volume of 250 cc at 50 percent relative humidity and 25°C will contain approximately 2.5 mg of water, which appears as ice in the collection trap. The possibility that ice will plug the trap and stop the sample flow is of concern; furthermore, water transferred to the capillary column during the thermal desorption step may also cause plugging and other deleterious column effects. Nonetheless, this limitation has not diminished research efforts to characterize the ambient atmosphere.

In addition to direct sampling via preconcentration with sorbents and cryogenic techniques, collection of whole air samples is frequently used to obtain NMOC data. Rigid devices such as syringes, glass bulbs, or metal containers; and non-rigid devices such as Tedlar and Teflon plastic bags are often utilized during sampling. The primary purpose of whole air collection is to store an air sample temporarily until subsequent laboratory analysis is performed. The major problem with this approach is assuring the integrity of the sample contents prior to analysis. Of concern is whether sample components of interest are adsorbed or decomposed through interaction with the container walls. Sample condensation may also occur at elevated concentrations or when samples are stored under high pressures (i.e., in metal containers). Contamination from sampling containers is likewise a frequent occurrence (Lonneman et al., 1981; Seila et al., 1976). Table 3-6 summarizes the advantages and disadvantages of the primary collection media for NMOC analysis.

3.3.1.1.3 Calibration. Calibration procedures for NMOC instrumentation require the generation of dilute mixtures at concentrations expected to be found in ambient air. Methods for generating such mixtures are classified as static or dynamic systems.

Static systems are generally preferred for quantitating NMOCs. The most commonly used static system is a compressed gas cylinder containing the appropriate concentration of the compound of interest. These cylinder gases may also be diluted with hydrocarbon-free air to provide multi-point calibrations. Calibration and hydrocarbon-free air cylinders are available commercially. Additionally, some standard gases such as propane and benzene are available from the National Bureau of Standards (NBS) as certified standard reference

TABLE 3-6. SUMMARY OF ADVANTAGES AND DISADVANTAGES OF PRIMARY COLLECTION MEDIA FOR NMOC ANALYSIS[a]

Sampling technique	Advantages	Disadvantages
1. Solid adsorbents	o Many sorbents do not retain H_2O vapor; thus, large volumes of air can be processed. o Integrated samples from a period of minutes to days are easily obtained. o Sample cartridges are convenient for field use.	o No single adsorbent can be used to collect and recover organics of C_2 and above. o Contamination and artifact peaks plague many sorbent systems. o Many adsorbents require high (>300°C) thermal desorption temperatures, which may lead to degradation of labile compounds, artifact peak formation, etc. o Breakthrough volume and collection and recovery efficiencies must be determined for each compound of interest.
2. Cryogenic preconcentration	o A wide range of organic material can be collected. o Artifact problems are avoided. o Collected organics are immediately available for analysis, without solvent removal or use of high thermal desorption temperatures. o Collected species are stable; good recovery efficiencies are obtained.	o Volume of air collected is limited by amount of moisture condensing. o Liquid argon or oxygen is necessary for preconcentration.

TABLE 3-6. SUMMARY OF ADVANTAGES AND DISADVANTAGES OF PRIMARY COLLECTION MEDIA FOR NMOC ANALYSIS[a] (continued)

Sampling technique	Advantages	Disadvantages
3. Rigid containers (Metal canisters)	o Can be treated to make them chemically unreactive.	o High initial cost.
	o Durable; easy to clean, transport, and use.	o Limited collection volume.
	o Can be pressurized; leakage and permeation minimized.	o Difficult to collect integrated samples.
	o Excellent stability for many trace species; long-term storage is possible.	
4. Non-rigid containers (Teflon and Tedlar Bags)	o Readily available.	o Subject to breakage (at seams) during handling.
	o Convenient for collecting integrated samples.	o Admits sunlight.
	o Good short-term stability of trace species.	o Slow permeation of chemicals out of and into plastic bags during storage.
		o Outgassing contamination from bag material.
		o Short storage life.

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[a] Derived from Singh (1980); Jayanty and McElroy (1982); Sexton et al. (1981); National Academy of Sciences (1976); Lonneman et al. (1981); Holdren et al. (1982).

materials (SRM). Commercial mixtures are generally referenced against these NBS standards. In its recent technical assistance document for operating and calibrating continuous NMOC analyzers, the U.S. Environmental Protection Agency (1981b) recommended propane-in-air standards for calibration. Some commercially available propane cylinders have been found to contain other hydrocarbons (Cox et al., 1982), so that all calibration data should be referenced to NBS standards.

Because of the uniform carbon response of a GC-FID system (±10 percent) to hydrocarbons (Dietz, 1967), a common response factor is assigned to identified and unknown compounds obtained from the speciation systems. In cases where these compounds may be oxygenated species, an underestimation of the actual concentrations will be reported. In order to attain better accuracy, relative response factors for substituted hydrocarbons should be experimentally determined. In determining these factors, dynamic calibration systems (permeation tubes, diffusion tubes, syringe delivery systems) are normally employed to generate *in situ* known concentrations of the individual compound of concern. Although the GC-FID response has been found to be unchanged over a period of many months, it is recommended that single-point calibration checks be performed daily to assure the highest quality of the data. Weekly multi-point calibrations are sufficient during normal field programs.

3.3.1.1.4 *Comparison of non-speciation versus speciation methods*. Speciation methods involving cryogenic preconcentration (section 3.3.1.1.2) have been compared with commercially available or prototype continuous NMOC analyzers in the following studies.

Jayanty et al. (1982) conducted a laboratory comparison between the prototype non-speciation method described earlier (section 3.3.1.1.1) and their gas chromatographic separation method. Comparison of the two methods for 12 ambient air samples collected in stainless steel canisters showed agreement within ±15 percent. Ambient air concentrations ranged from 100 to 1000 ppb C.

Lonneman (1979) compared total NMOC and speciation methods during field studies in Houston in 1978. Samples were collected during 3-hour integrated time periods (6 to 9 a.m., 1 to 4 p.m.) in Tedlar bags for subsequent analysis. The correlation coefficients for 150 measurement pairs from five sites averaged 0.74. For data pairs of 500 ppb C and less, an average correlation coefficient (r^2) of 0.55 was calculated, with a low value of 0.12 at one site. Lonneman attributed the low correlations to maintenance and calibration problems in the continuous analyzers and concluded that the results from continuous analyzers are "at best marginal for use in photochemical model applications."

Holdren et al. (1982) made a similar comparison during a 2-month study at urban sites in Cincinnati and Cleveland, Ohio. They utilized a GC/cryogenic trapping technique and compared their results with data from state-operated NMOC analyzers (SAROAD data). Ambient air samples were collected in Teflon bags (6 to 9 a.m. integrated collection) and were transferred immediately to pretreated aluminum cylinders for shipment and analysis at the central laboratory. Concentrations of NMOC ranged from 200 to 2100 ppb C. Linear regression analyses resulted in correlation coefficients that ranged from 0.75 to 0.92 for the four urban sites (total of 67 comparisons). Limiting the comparisons to concentrations of 500 ppb C and lower resulted in an average correlation coefficient of 0.10 (at all four sites).

Richter (1983) compared continuous total NMOC with GC speciation results obtained at seven fixed ground-level sites used in the Northeast Corridor Regional Modeling Project (NECRMP). The NMOC data were obtained in real time, while Teflon bags were used to collected integrated samples (6 to 9 a.m.) for the GC/cryogenic analyses. Over 60 comparisons were available from each site. Table 3-7 summarizes statistical information obtained from least-squares analysis of the data (Richter, 1983). As the table indicates, only data from the East Boston site exhibited a high correlation coefficient. This study represents the most extensive effort made yet to compare the two NMOC measuring methods. The participating laboratories paid a great deal of attention to technical details for correct instrument operation, calibration, etc. All data were carefully examined by all contractors and only "verified" data were compared. Yet the above results indicate that much more work is needed to resolve the differences between the two methods.

3.3.1.2 Aldehydes. Aldehydes play a unique role in the photochemistry of the troposphere. They contribute to the formation of photochemical oxidants as precursors to free radicals and occur as products of the photooxidation of gas-phase hydrocarbons, often as chain terminators. Aldehydes appear to be second in abundance, next to nonmethane hydrocarbons, among classes of volatile organic compounds found in ambient air. Historically, the major problem in measuring concentrations of aldehydes in ambient air has been to find an appropriate monitoring technique that is sensitive to low concentrations and specific for the various homologues. Early techniques for measuring formaldehyde, the most abundant aldehyde, were subject to many interferences and

TABLE 3-7. GC/CONTINUOUS NMOC ANALYZER COMPARISONS, LEAST-SQUARES REGRESSIONS

Location	Slope	Intercept, ppm C	Standard error	r^2
West End Library, Washington, DC	0.562	-0.582	0.672	0.168
Read Street, Baltimore, MD	0.443	-0.283	0.743	0.0077
Essex, MD	0.835	-0.101	0.599	0.384
Linden, NJ	0.531	--	0.865	0.141
Newark, NJ	0.987	-0.277	0.574	0.467
East Boston, MA	1.108	+0.095	0.327	0.887
Watertown, MA	0.750	-0.568	0.574	0.475

Source: Richter, 1983.

lacked sensitivity at low concentrations. When used by skillful technicians, the more recently developed techniques can characterize with relative accuracy the types and amounts of aldehydes in ambient air. This section describes those methods currently used for measuring aldehydes in ambient air. These include the chromotropic acid (CA) method for formaldehyde, the 3-methyl-2-benzothiazolone (MBTH) technique for total aldehydes, Fourier-transform infrared (FTIR) spectroscopy, and the high-performance liquid chromatography (HPLC) method employing 2,4-dinitrophenylhydrazine (DNPH) derivatization.

3.3.1.2.1 Chromotropic acid method. The chromotropic acid method (CA) involves the collection of formaldehyde in a midget impinger containing an aqueous mixture of chromotropic and sulfuric acids, followed by the spectrophotometric measurement of absorbance of the resulting color (Altshuller and McPherson, 1963; U.S. Dept. of Health, Education and Welfare, 1965). A modification described by Johnson et al. (1981) improved the accuracy and sensitivity of the CA method by reducing the concentration of sulfuric acid and by eliminating a heating cycle, relying solely on the heat of solution generated by sulfuric acid (Altshuller et al., 1961; Olansky and Deming, 1976). Trapping formaldehyde in a 1 percent bisulfite solution before adding the CA solution increased collection efficiency from 84 percent to 92 percent with no sulfite interferences.

The CA method for measuring formaldehyde has been widely studied (Salas and Singh, 1982; Grosjean and Kok, 1981; National Academy of Sciences, 1981; Tuazon et al., 1980; Lloyd, 1979). Originally developed as a spot test by Eegriwe (1937), it was adapted to quantitate formaldehyde spectrophotometrically (Bricker and Johnson, 1945; West and Sen, 1956) and was modified for ambient air measurements in the early 1960s (Altshuller et al., 1961; Altshuller and McPherson, 1963; U.S. Dept. of Health, Education, and Welfare, 1965). While used widely today for both occupational and ambient air environments, its specificity for formaldehyde, which accounts for approximately half of total ambient air aldehydes (see section 3.3), limits its usefulness for characterizing aldehyde concentrations in ambient air.

The CA method has been reported to be sensitive to acrolein, acetaldehyde, phenol, nitrogen dioxide, and nitrates (National Academy of Sciences, 1981; Krug and Hirt, 1977; U.S. Dept. of Health, Education, and Welfare, 1973; Sleva, 1965; Altshuller et al., 1961). Recent work, however, indicates that neither nitrates, nitrites, NO_2, nor acetaldehyde at elevated ambient air levels interfere with the CA analysis (Johnson et al., 1981; Grosjean and Kok, 1981). Relevant data on other interfering agents were not found.

3.3.1.2.2 MBTH method. A spectrophotometric technique for total aldehydes was developed in the early 1960s by Sawicki and coworkers (1961). Known as the MBTH method, it involves the reaction of aldehyde with 3-methyl-2-benzothiazolone hydrazone to form an azine that is oxidized by a ferric chloric-sulfamic acid solution to form a blue cationic dye (Altshuller, 1983a; U.S. Dept. of Health, Education, and Welfare, 1965; Hauser and Cummins, 1964; Altshuller and McPherson, 1963; Altshuller and Leng, 1963; Altshuller et al., 1961).

The MBTH method has a reported sensitivity of 15 ppb for, primarily, low-molecular-weight aldehydes (National Academy of Sciences, 1981). The method is subject to interferences by NO_2 and gives an inconsistent response to higher-molecular-weight aldehydes (Sawicki et al., 1961; Altshuller et al., 1961). Nonetheless, the Intersociety Committee of the American Public Health Association recommends the MBTH colorimetric method for determining total aldehydes in air (American Public Health Association, 1977). Miksch and Anthon (1982) devised a sampling and analysis scheme that permitted a single

MBTH sample to be used for both formaldehyde and total aliphatic aldehyde determinations.

3.3.1.2.3 Fourier-transform infrared spectroscopy. Infrared absorption spectroscopy has been used by several groups to identify and measure aldehydes in ambient air (Hanst et al., 1982; Tuazon et al., 1978, 1980, 1981b; Hanst et al., 1975). These studies employed Fourier-transform infrared (FT-IR) spectrometers interfaced to multiple reflection cells operating at total optical paths of up to 1 km. At such pathlengths, a detection limit of a few ppb was achieved for formaldehyde. The advantages of the long-pathlength FT-IR method for ambient air aldehyde measurements (i.e., good specificity and direct *in situ* analysis) are offset by the relatively high cost and lack of portability of such systems.

3.3.1.2.4 High-performance liquid chromatography (HPLC) 2,4-dinitrophenylhydrazine (DNPH) method. This method takes advantage of the long-established reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine to form a 2,4-dinitrophenylhydrazon:

$$RR'C{=}O + NH_2NHC_6H_3(NO_{22} \qquad H_2O + RR'C = NNHC_6H_3(NO_2)_2 \quad (3\text{-}1)$$

Since DNPH is a weak nucleophile the reaction is carried out in the presence of acid in order to increase proonation of the carbonyl.

The HPLC-DNPH method is curently the preferred way of measuring aldehydes in ambient air. Atmospheric sampling is usually conducted with micro-impingers containing an organic solvent and aqueous, acidified DNPH reagent (Papa and Turner, 1972; Katz, 1977; Cadle, 1979; Smith and Drummond, 1979; Fung and Grosjean, 1981). After sampling is completed, the hydrazone derivatives are extracted and the extract is washed with deionized water to remove the remaining acid and unreacted DNPH reagent. The organic layer is then evaporated to dryness, subsequently dissolved in a small volume of solvent, and analyzed by reversed-phase liquid chromatographic techniques employing an ultraviolet (UV) detection system.

Recently, an improved procedure has been reported that is much simpler than the above aqueous impinger method (Lipari and Swarin, 1982; Kuntz et al., 1980). This scheme utilizes a midget impinger containing an acetonitrile solution of DNPH and an acid catalyst. After sampling, an aliquot of the original collection solution is directly injected onto the chromatograph.

This approach eliminates the extraction step and several sample-handling procedures associated with the DNPH-aqueous solution; and provides much better recovery efficiencies. Lipari and Swarin (1982) have reported detection limits of 20, 10, 5, and 4 ppb for formaldehyde, acetaldehyde, acrolein, and benzaldehyde, respectively, in 20-liter air samples.

3.3.1.2.5 Calibration of aldehyde measurements. Since they are reactive compounds, it is extremely difficult to make stable calibration mixtures of aldehydes in pressurized gas cylinders. Although gas-phase aldehyde standards are available commercially, the vendors do not guarantee any level of accuracy.

Formaldehyde standards are generally prepared by one of several methods. The first method utilizes dilute commercial formalin (37 percent formaldehyde, w/w). Calibration is accomplished by the direct spiking into sampling impingers of the diluted mixture or by evaporation into known test volumes, followed by impinger collection. Formaldehyde can also be prepared by heating known amounts of paraformaldehyde, passing the effluent gases through a methanol-liquid nitrogen slush trap to remove impurities, and collecting the remaining formaldehyde.

For the higher-molecular-weight aldehydes, liquid solutions can be evaporated or pure aldehyde vapor can be generated in dynamic gas-flow systems (permeation tubes, diffusion tubes, syringe delivery systems, etc.). These test atmospheres are then passed through the appropriate aldehyde collection system and analyzed. A comparison of these data, with the direct spiking of liquid aldehydes into the particular collection system, provides a measure of the overall collection efficiency.

3.3.1.2.6 Comparison of measurement methods. Several side-by-side comparisons of the chromotropic acid method (CA) with other methods have been reported. Grosjean and Kok (1981) compared the CA method (Johnson et al., 1981) with HPLC-DNPH (Fung and Grosjean, 1981) and FTIR spectroscopy (Tuazon et al., 1978). They found fairly close agreement between the CA and HPLC-DNPH methods, but noted consistently higher results with FTIR. Corse (1981) sampled ambient air with CA (U.S. Dept. of Health, Education, and Welfare, 1965), MBTH (U.S. Dept. of Health, Education, and Welfare, 1965), and HPLC-DNPH methods (Kuntz et al., 1980). An examination of tabulated data from the Corse study shows a consistent and considerable difference between CA and HPLC measurements. For 25 CA measurements, formaldehyde averaged 8.8 ppb; while HPLC measurements from the same sampling train averaged 5.4 ppb higher. Overall, formaldehyde levels were approximately 60 percent higher with HPLC than with CA measurements. Because blanks were not utilized for the HPLC analyses, however, the HPLC data are subject to uncertainty, since blank corrections can affect results substantially (Altshuller, 1983). During laboratory studies, Kuntz et al. (1980) reported reasonable agreement (±7%) among the HPLC-DNPH, CA, and FTIR methods when low ppb levels of formaldehyde, acetaldehyde, propionaldehyde, hexanal, and benzaldehyde were generated.

3.3.1.3 Other Oxygenated Organic Species. Literature reports describing the vapor-phase organic compounds occurring in ambient air indicate that the major fraction of material consists of unsubstituted hydrocarbons (section 3.5). Aldehydes as a class of volatile organics appear second in abundance. With the exception of formic acid (Hanst et al., 1982; Tuazon et al., 1981, 1980, 1978), other oxygenated species are seldom reported. The lack of oxygenated hydrocarbon data is somewhat surprising since significant quantities of these species are emitted directly into the atmosphere by solvent-related industries (methanol, ethanol, acetone, etc.; see section 3.4). Along with manmade emissions, natural sources of oxygenated hydrocarbons also contribute to this total. In addition to direct emissions, it is also expected that photochemical reactions of hydrocarbons with oxides of nitrogen, ozone, and hydroxyl radicals will produce significant quantities of oxygenated products.

Difficulties in sample collection and analysis may account for this apparent lack of data. The adsorptive nature of the surfaces that contact these oxygenated species often complicates the process of compound quantitation. Presently, the approach used for analysis of oxygenated and other polar organic compounds has been to decrease adsorption by deactivating the interior surfaces of analytical hardware. A novel method has been reported in which the reactive compounds of interest were modified rather than the surfaces with which these compounds interact (Osman et al., 1979; Westberg et al., 1980). In these studies, the laboratory derivatization of vapor-phase alcohols and acids (silylation) was investigated to evaluate the potential of such a procedure for stabilizing these polar compounds prior to analysis. Results have indicated that silylation procedures greatly reduced adsorption of alcohols and acids and that, qualitatively, the silylated derivatives could be detected via the GC-F1D system.

3.3.2 Nitrogen Oxides

Aside from the essentially unreactive N_2O, only two oxides of nitrogen occur in ambient air at appreciable concentrations, nitric oxide (NO) and nitrogen dioxide (NO_2). Both compounds, together designated as NO_x, participate in the cyclic reactions in the atmosphere that lead to the formation of ozone (section 4.2).

Analytical methods for NO_2 and NO that are in current use are briefly described in this section. Older methods, including the former Federal Reference Method (Jacobs-Hocheiser method), are described in a recent criteria document on nitrogen oxides prepared by the U.S. Environmental Protection Agency (1982).

3.3.2.1 Measurement Methods for NO_2 and NO. In 1976, the continuous chemiluminescence method was promulgated as the new Federal Reference Method. Other acceptable methods for measuring ambient NO_2 levels, including two methods designated as equivalent methods, are the Lyshkow-modified Griess-Saltzman method, the instrumental colorimetric Griess-Saltzman method, the triethanolamine method, the sodium arsenite method, and the TGS-ANSA method [TGS-ANSA = triethanolamine, guaiacol (o-methoxyphenol), sodium metabisulfite, and 8-anilino-1-naphthalene sulfonic acid]. The sodium arsenite method and the TGS-ANSA method were designated as equivalent methods in 1977. While some of these methods measure the species of interest directly, others require oxidation, reduction, or thermal decomposition of the sample, or separation from interferences, before measurement. Table 3-8 presents a summary of these methods.

The current Federal Reference Method measures atmospheric concentrations of NO_2 indirectly by first reducing or thermally decomposing the gas quantitatively to NO (with a converter), reacting NO with O_3, and measuring the light intensity from the chemiluminescent reaction. Two types of converters have been employed for converting NO_2 to NO. The first type, e.g., a carbon converter, actually reduces the NO_2 to NO. The second, e.g., hot stainless steel, thermally decomposes the NO_2, producing NO. Interfering species will depend on the type of converter used. The reaction of NO and O_3 forms electronically excited NO_2 molecules that release light energy that is proportional to the NO concentration (Fontijn et al., 1970). The NO in the air stream is measured separately and subtracted from the previous NO_x (NO plus NO_2) measurement to yield the NO_2 concentration. Typical commercial chemiluminescence instruments are

TABLE 3-8. METHODS FOR MEASURING NITROGEN DIOXIDE[a]

Name	Description	Figures of merit	Reference
Chemiluminescence	NO_2 is converted to NO; NO is reacted with O_3, emitting light. Designated as the Federal Reference Method.	Lower detection limit is 2.5 μg/m^3 (0.002 ppm). Suitable for $\geq$1-hr averaging times. Average negative bias of $\sim$5% with S.D. ± 14% of measured value for 1-hr averaging time and range of 50 to 300 μg/m^3 (0.027 to 0.16 ppm).	Katz (1976); and U.S. Environmental Protection Agency (1976a,b) Constant et al. (1974)
		PAN and other nitrogen compounds, including nitroethane and nitric acid (HNO_3) may be converted to NO.	Winer et al. (1974)
		Ammonia may be converted to NO if high-temperature converter is used.	U.S. Environmental Protection Agency (1982)
		Halocarbons may interfere, if heated carbon converter is used.	Joshi and Bufalini (1976)
		HNO_3 and PAN can cause appreciable overestimation of NO_2 during smog conditions.	Spicer (1977a); and Grosjean (1982b)
Griess-Saltzman	NO_2 reacts with water to form nitrous acid, which is reacted with an aromatic amine to form a diazonium salt, to which an organic coupling agent is added to form an azo dye. The amount of NO_2 collected is related to absorbence of the solution. Considered suitable for averaging times >1 hr.	Usable range: 19 to 9400 μg/m^3 (0.01 to 5.0 ppm) Maximum negative bias among different laboratories testing equivalent samples: 15%, with S.D. of ± 12% of average value.	Saltzman (1954); and Constant et al. (1975)

TABLE 3-8. METHODS FOR MEASURING NITROGEN DIOXIDE[a] (continued)

Name	Description	Figures of merit	Reference
Triethanolamine	NO_2 is absorbed in a solution of triethanolamine and *n*-butanol surfactant; analyzed by Griess-Saltzman reagent, producing an azo dye for spectrophotometric measurement. Considered suitable as a 24-hr method.	Collection efficiency in the range of 30 to 700 μg/m³ (0.01 to 0.37 ppm): 1. When glass frits are used: 80%. 2. When restricted orifices are are used: 50%.	Ellis and Margeson, 1974
		Bias error at a stoichiometric factor of 0.764 is <2%.	Scaringelli et al., 1970
Sodium arsenite	Designated as an equivalent method, considered suitable for 24-hr measurement. NO_2 is absorbed in an alkaline solution of sodium arsenite, then acidified with phosphoric acid; azo dye is formed by addition of sulfanilamide N-(1-naphthyl) ethylenediamine dihydrochloride.	Collection efficiency from 20 to 750 μg/m³ (0.01 to 0.4 ppm): 82%	Beard and Margeson, 1974
		Negative bias among different laboratories testing equivalent samples: 3% with S.D. of ± 11 μg/m³.	Constant et al., 1975
		Increase in NO_2 response from NO in the range of 50 to 310 μg/m³ (0.04 to 0.25 ppm): maximum 10 μg/m³.	Beard et al., 1975
		Increase in NO_2 response from CO_2 in the range of 360,000 to 899,000 μg/m³ (200 to 500 ppm): 50 to 250 μg/m³ (0.02 to 0.13 ppm).	Beard et al., 1975

TABLE 3-8. METHODS FOR MEASURING NITROGEN DIOXIDE[a] (continued)

Name	Description	Figures of merit	Reference
TGS-ANSA	A 24-hr manual method, designated an equivalent method. Ambient air is bubbled through a solution of triethanolamine, o-methoxyphenol, and sodium metabisulfite. NO_2 is converted to nitrite ion, which is assayed by diazotization and coupling using sulfanilamide and the ammonium salt of 8-anilino-1-naphthalene-sulfonic acid. Absorbence is read at 500 nm. [TGS-ANSA = triethanolamine, guaiacol, sodium metabisulfite (TGS) and 8-anilino-1-naphthalene sulfonic acid (ANSA).]	Collection efficiency with addition of o-methoxyphenol: 95%	Nash, 1970; Fuerst and Margeson, 1974
		At NO_2 concentration of 100 µg/m³ (0.05 ppm); no interferences from ammonia (25 µg/m³); CO_2 (154,000 µg/m³); formaldehyde (750 µg/m³); NO (734 µg/m³); and SO_2 (439 µg/m³)	Fuerst and Margeson, 1974 Mulik et al., 1973
		Lower detection limit, <15 µg/m³ (0.008 ppm).	Constant et al., 1974
		Average bias over the range of 50 to 300 µg/m³ (0.03 to 0.16 ppm) is 9.5 µg/m³ (0.005 ppm).	
		Interlaboratory standard deviation is ± 8.8 µg/m³ (0.004 ppm).	

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[a] Adapted from U.S. Environmental Protection Agency (1982).

capable of detecting levels as low as 2.5 μg/m^3 (0.002 ppm) (Katz, 1976). Winer et al. (1974) found that peroxyacetyl nitrate (PAN) and various nitrogen compounds were also reduced by the converter to NO and that nitroethane and nitric acid were partially reduced in the system when carbon (reducing) converter or a molybdenum (thermal decomposition) converter was used. Joshi and Bufalini (1976) reported positive interferences from halocarbons when a heated carbon converter was used; they also suggested that stainless steel converters may be subject to interferences from chlorinated hydrocarbons. Other evidence suggests that ammonia (NH_3) may be converted to NO in high-temperature thermal converters (U.S. Environmental Protection Agency, 1982). Spicer et al. (1979) reported that positive interference with chemiluminescent NO_2 measurements can be significant under smoggy conditions. Positive interferences resulting from the presence of PAN and HNO_3 on afternoons of high oxidant concentrations can exceed 30 percent of the NO_2 concentrations. Grosjean (1982) also reported that positive interferences from nitric acid and PAN during NO_2 analysis by chemiluminescence can cause a 50- to 60-percent NO_2 overestimation during smog conditions in Los Angeles. In less severe smog, the overestimation should not be this high.

In addition to the wet chemical methods for measuring NO_2, other techniques have been investigated. Maeda et al. (1980) reported a new chemiluminescence method based on the reaction of NO_2 with luminol (5-amino-2,3-dihydro-1, 4-phthalazine dione), with a detection limit of about 50 parts per trillion (ppt) and linearity over a range of 0.5 ppb to 100 ppm. Work is under way to remove the interferences of O_3 and SO_2. Other workers have endeavored to improve chemiluminescence analyzers through physical modifications (Ridley and Howlett, 1974; Schiff et al., 1979; Stedman et al., 1977). Molecular correlation spectrometry, in which an absorption band of a sample is compared with a corresponding band stored in the spectrometer, has been applied in analysis of NO_2 (Williams and Kolitz, 1968). Instruments processing the second derivative of sample transmissivity have also been used (Hagar and Anderson, 1970), as have infrared lasers and infrared spectrometers (Hanst, 1970; Hinkley and Kelley, 1971; and Kreuzer and Patel, 1971). Tucker et al. (1973, 1975) reported on instruments based on the principle of laser-induced fluorescence at optical frequencies. Fincher et al. (1977) described detection of 1 ppb NO_2 with a technique based on fluorescence by a pulsed xenon flashlamp. Long-pathlength differential optical absorption spectroscopy has also been employed to monitor NO_2 in the troposphere (Platt et al., 1984; 1980).

As summarized from the criteria document for nitrogen oxides prepared by the U.S. Environmental Protection Agency (1982), methods for measuring NO directly include ferrous sulfate absorption and spectrophotometric measurement of the resulting ion (Norwitz, 1966), ultraviolet spectroscopy (Sweeny et al., 1964), and infrared spectroscopy (Lord et al., 1975). Mass spectrometry and gas chromatography may also be employed. None of the above techniques, however, is widely used to monitor air quality. The best direct method for measuring NO is chemiluminescence, employing ozone as the reactant (equation 4-3, chapter 4) (Fontijn et al., 1970).

3.3.2.2 Sampling Requirements. When sampling for NO_x, long residence times in sampling lines should be avoided. In the ambient air, the rate of photolysis of NO_2 (forming NO and O, and thus O_3) is almost equal to the rate of the reaction of the NO and O_3 to form NO_2. In sampling lines, photolysis stops but NO continues to react with O_3, producing NO_2. The magnitude of the dark reaction of NO with O_3 depends, of course, on the concentrations of NO and O_3 in the sample being analyzed, as well as on the residence time of the sample in the line. This dark reaction has greater practical consequences in some situations than in others. In moderately polluted urban areas, steady-state concentrations of NO are almost certainly too low at the period of maximal O_3 to cause significant errors in obtaining NO_x or O_3 measurements. Conversely, when O_3 is at a minimum, as in the early morning or possibly even in the late afternoon, NO (and NO_2) may be at maximal levels, and no significant errors would be introduced. If the concentrations of NO and O_3 are both low, however, as in some rural areas, or during those brief periods in polluted areas when NO and O_3 diurnal patterns cross, then significant measurement errors could be introduced. Values for NO_2 would be erroneously high and values for O_3, if simultaneous measurements of O_3 were being attempted, would be erroneously low.

Techniques for limiting errors from sampling to given levels of tolerance are reviewed by Butcher and Ruff (1971). In general, only glass or Teflon materials should be used in sampling trains. Among absorbents, granules impregnated with triethanolamine are reported to be the best, converting only 2 to 4 percent of the incoming NO_2 to NO (Intersociety Committee, 1977; Huygen, 1970). The most frequently used oxidizer is chromic oxide on a fire-brick granule support (Intersociety Committee, 1977; Levaggi et al., 1974).

3.3.2.3 Calibration. Procedures for calibrating measurement methods used to determine NO_x are critical for obtaining accurate analyses. Monitoring instruments may be calibrated either by measuring a gas of known concentration or by comparing measurements of gas from a stable source with measurements made by a primary reference method. Measurement methods for NO and NO_2 are calibrated principally by standard reference materials (SRM). In a National Bureau of Standards study, the initial accuracy and stability of standard mixtures of NO in nitrogen were found to be high (Hughes, 1975). Other sources include permeation of compressed NO through membranes to produce dilute NO streams (U.S. Environmental Protection Agency, 1976), electrolytic generation (Hersch and Deuringer, 1963), catalytic reduction of NO_2 (Breitenbach and Shelef, 1973), and photolysis and rapid dilution of NO_2 (Guicherit, 1972). Of these standard reference materials, only compressed NO and the NO_2 permeation tube are currently used. The U.S. Environmental Protection Agency (1976a,b) recommended the combined use of permeation tubes and gas-phase titration, using one technique to check the other. The two standard reference materials available for generating known concentrations of NO and NO_2 are the cylinder of compressed NO in N_2 (50 and 100 ppm) and the NO_2 permeation tube. Both are commercially available and are traceable to SRMs at the National Bureau of Standards.

The preparation of standard mixtures of NO in nitrogen has been studied by the National Bureau of Standards (Hughes, 1975). The initial accuracy with which standards may be prepared, based on either pressure or mass measurements, is quite good. The stability of mixtures at concentrations above about 50 ppm was found to be satisfactory; the average change in concentrations over a 7-month period was only 0 to 1 percent.

The permeation tube is the only direct source of dilute NO_2 mixtures in widespread use (O'Keefe and Ortman, 1966; Scaringelli et al., 1970). It may be calibrated by weighing or, though rarely done, by micromanometric measurements. The other common procedure used to calibrate NO_2 measurement instruments is gas-phase titration. Stable sources of known concentrations of both NO and O_3 are required. A dilute stream of NO is measured by NO methods. The O_3 is added to the stream at a constant rate. The decrease in NO that occurs through its reaction with the added ozone is equal to the NO_2 formed. Thus, a known NO_2 concentration is produced.

3.4 SOURCES AND EMISSIONS OF PRECURSORS

3.4.1 Manmade Sources and Emissions

This section presents information on the manmade sources and emissions of precursors to ozone and other photochemical oxidants. There are no major or pervasive primary sources of ozone or of related photochemical oxidants. In isolated instances, intrusion of stratospheric ozone into the troposphere may briefly make a significant local contribution to the natural background con-concentration of ground-level ozone (chapter 4). Human activities generate no significant direct contribution to ambient ozone concentrations. Consequently, ozone and other photochemical oxidants are almost exclusively secondary pollutants arising from the emission and reactions of primary pollutants.

It should be noted that the relationship between emissions of the precursors and the resulting ozone levels is neither direct nor constant. Thus, the magnitudes of source emissions cited here are best viewed as indicating a potential for ozone production rather than as determining or predicting the extent of the ozone problem in any particular area.

Three recent documents, which have been extensively reviewed by the scientific community, discuss sources of nitrogen oxides, aldehydes, and hydrocarbons and other volatile organic compounds. These are Air Quality Criteria for Oxides of Nitrogen (U.S. Environmental Protection Agency, 1982); Formaldehyde and Other Aldehydes (National Academy of Sciences, 1981); and Review of Criteria for Vapor-Phase Hydrocarbons (Tilton and Bruce, 1981). Wherever appropriate, material is quoted from these documents; updated material is included in the few cases in which significant new information has appeared since their publication.

Many volatile organic compounds besides hydrocarbons may participate in photochemical smog reactions. The Federal reference method for nonmethane hydrocarbons uses a flame ionization detector as the sensing element, which is not specific for hydrocarbons but also responds to varying degrees to other nonmethane organic compounds (section 3.3). For these reasons, the U.S. Environmental Protection Agency has, in recent years, subsumed hydrocarbon source and emissions data into the broader category of volatile organic compounds (VOC). Several compounds are deliberately excluded because their contribution to the production of photochemical oxidants in the lower troposphere is considered negligible. The principal compound, methane, constitutes a significant fraction of hydrocarbons in ambient air; the others, ethane, methylene chloride, and several halomethanes and haloethenes, are also excluded from emission inventories (U.S. Environmental Protection Agency, 1980b).

The preparation of an emission inventory involves the compilation of a series of estimates and thus is subject to the errors inherent in any inventory. There are two broad categories of emission inventories: (1) collective nationwide estimates based on average annual emissions in the respective general source categories; and (2) detailed inventories prepared for the purpose of developing control strategies. The latter is prepared for specific localities, such as a metropolitan area, and accounts for influences such as industries that are seasonal, and local meteorology. The data discussed here are in the first category and were compiled for the purpose of identifying nationwide trends. In these collective, annual, nationwide inventories, random error components will tend to cancel out, but systematic error or bias will remain. The direction of this systematic error is probably toward the low side because of overlooked sources. This does not impair the use of these estimates for trend analysis, because as the inventory procedures have been refined, estimates for prior years have been recalculated. Thus, the discussion of trends in emissions below is based on data in which the remaining biases are consistent for all years.

Inventories for VOC emissions are less reliable than those for most of the criteria pollutants. Emission inventory procedures for stationary sources were originally developed to estimate emissions of particulate matter and sulfur dioxide. As inventories for additional pollutants were compiled, existing procedures were applied without much change. In some cases, this was appropriate (e.g., for oxides of nitrogen). Because of the nature of VOC sources, which produce a higher percentage of fugitive emissions that are hard to account for, the use of historical procedures for VOC emission sources has been found to be generally inadequate. Improved procedures have recently been developed that account more completely for emissions from the ubiquitous sources of VOC (U.S. Environmental Protection Agency, 1980a).

These annual emission estimates cannot be scaled to shorter time periods or to individual areas of the country because seasonal variations occur in some source emissions and because the roster of sources obviously varies from city to city. The second type of emission inventory mentioned above is applicable where attention to these details is required (U.S. Environmental Protection Agency, 1981).

3.4.1.1 Trends in Emissions of Volatile Organic Compounds. Although not all volatile organic compounds have the same potential for oxidant formation, estimates of their total emissions nevertheless provide a gross measure of compounds available for photochemical production of ozone and other photochemical oxidants. Figure 3-3 shows national trends in emissions of volatile organic compounds (VOC) by general source category for the period 1970 through 1981. Total VOC emissions nationwide were 22 percent lower in 1981 than in 1970. The main sources nationwide are industrial processes, which emit a wide variety of VOCs such as chemical solvents; and transportation, which involves the emission of VOCs in gasoline vapor as well as in gasoline combustion products. Industrial process emissions peaked in 1978 and 1979, while emissions from transportation sources decreased about 35 percent despite a 42-percent increase in total vehicle miles driven. Decreases also occurred in the solid waste and miscellaneous categories.

3.4.1.2 Trends in Emissions of Nitrogen Oxides. Total national NO_x emissions in 1982 were almost 12 percent above the 1970 rate, but appear to have declined slightly from 1978 and 1979 levels (Figure 3-4). The increase over the period 1970 through 1982 may be attributed primarily to two causes: (1) increased fuel combustion in stationary sources such as power plants; and (2) increased fuel combustion in highway motor vehicles, as the result of the increase in vehicle miles driven. Total vehicle miles driven increased by 42 percent over the 13 years in question. Emissions associated with industrial processes remained relatively constant, but solid waste and miscellaneous emissions decreased slightly.

The national trends shown do not reflect the considerable local and regional differences that exist in the relative amounts of NO_x emitted in the major source categories. For example, motor vehicle emissions in Los Angeles County, California, increased sixfold from 1940 to 1970 (Los Angeles County, 1971), compared to a threefold national increase.

Although they are minor on a national level, industrial process losses (NO_x emissions from noncombustion industrial sources) can be important near individual local sources. The principal activities in this source category are petroleum refining and the manufacture of nitric acid, explosives, and fertilizers.

Aircraft are not considered a major source of NO_x on the national scale, but their impact in the immediate vicinity (at a radius of up to 10 miles) of

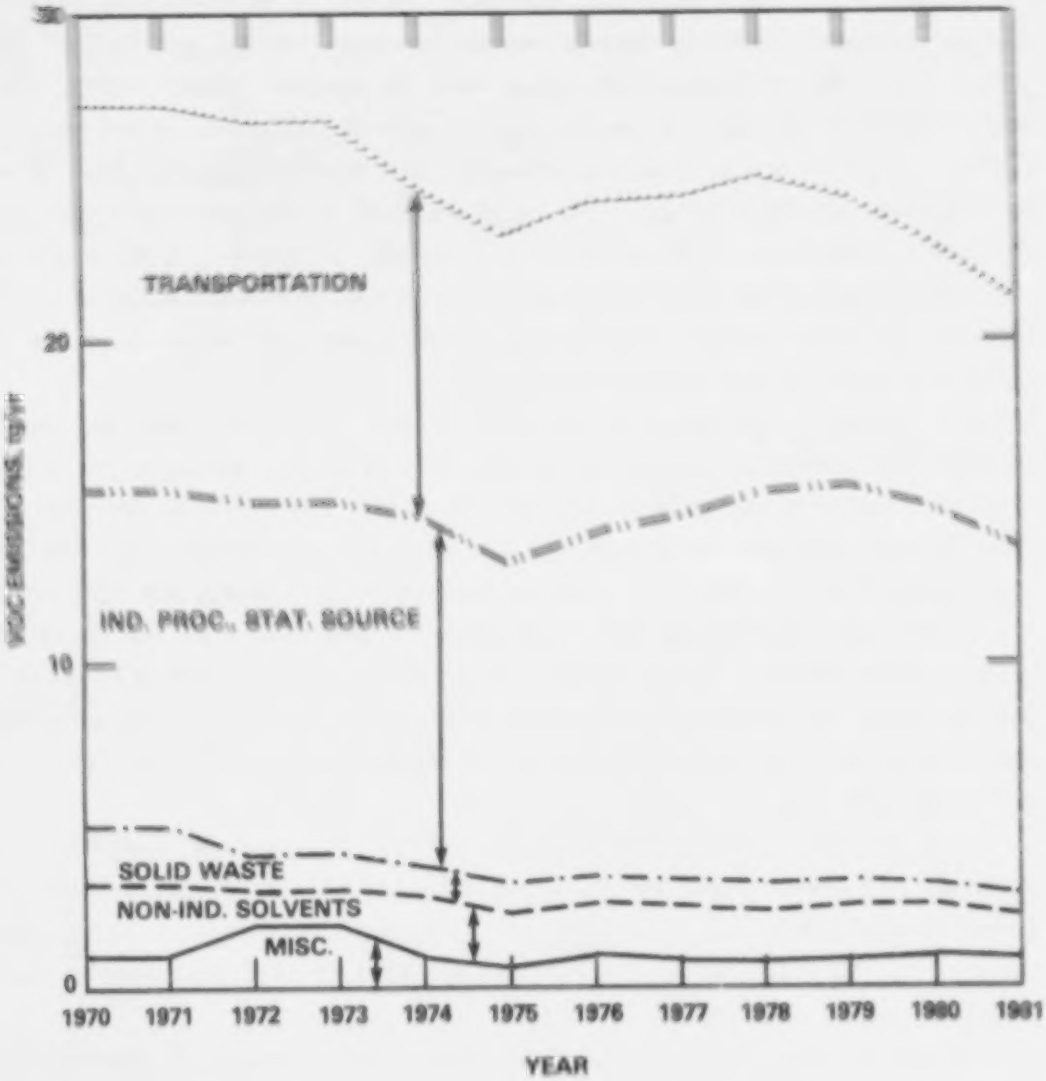

Figure 3-3. National trend in estimated emissions of volatile organic compounds, 1970 through 1982.

Source: U.S. Environmental Protection Agency (1982b).

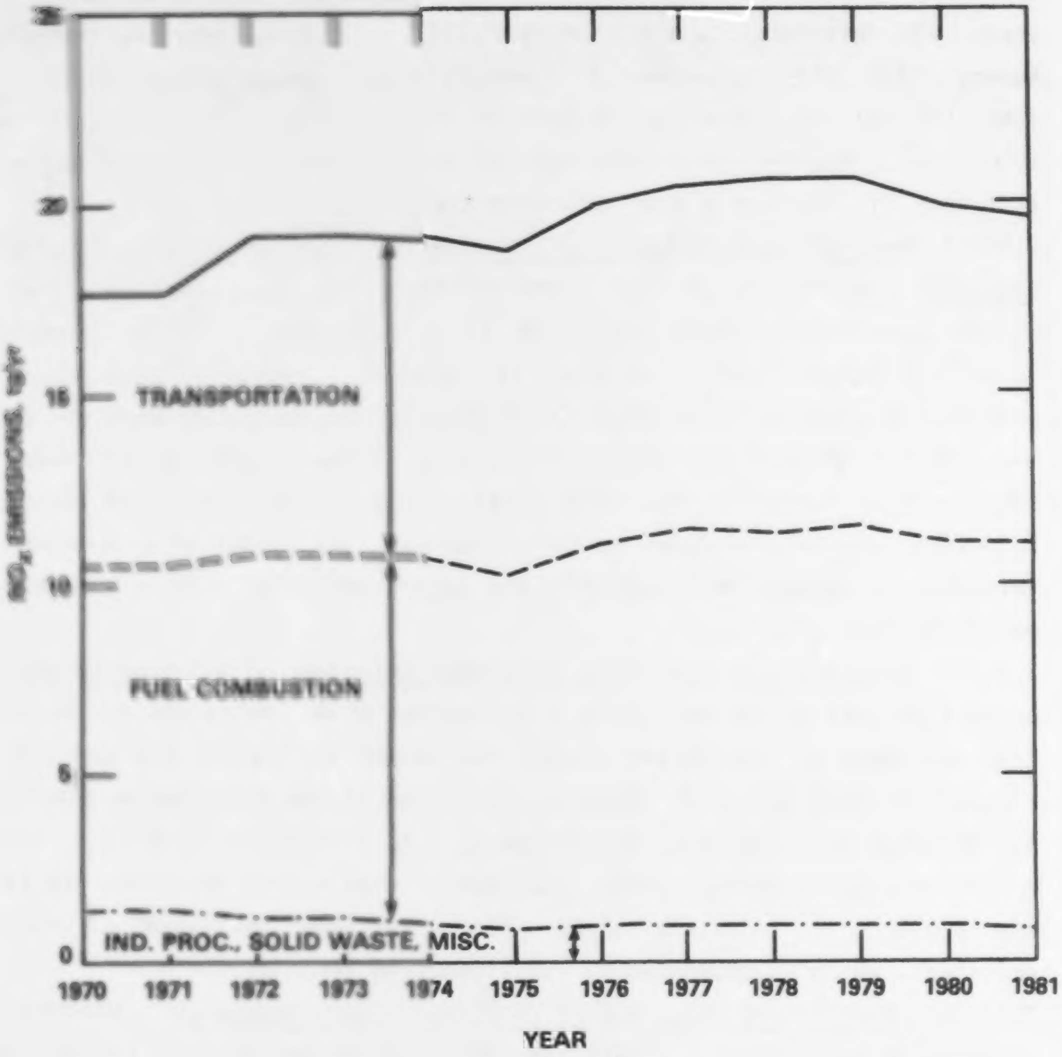

Figure 3-4. National trend in estimated emissions of nitrogen oxides, 1970 through 1982.

Source: U.S. Environmental Protection Agency (1982b).

major airports has been discussed by George et al. (1972) and by Jordan and Broderick (1979).

Figure 3-5 compares the relative trends in mobile source NO_x and VOC emissions versus the trend in vehicle miles traveled, both total and in urban areas, all referenced to the base year 1970 (U.S. Environmental Protection Agency, 1983; U.S. Department of Transportation, annual publications). By 1982, VOC emissions from mobile sources were only about 60 percent of their 1970 level. Mobile source emissions of NO_x were about 28 percent higher in 1981 than in 1970, but a small downward trend began in 1979.

3.4.1.3 Geographic Distribution of Manmade Emissions of Volatile Organic Compounds. An overall picture of the density of VOC emissions for all counties in the coterminous United States, as of February 1978 (U.S. Environmental Protection Agency, 1978), is given in Figure 3-6. Areas of high emission density are apparent in Southern California; in the Northeast Corridor extending from the greater Washington, D.C., area to the greater Boston area; in many counties bordering the Great Lakes; along the Gulf Coast of Texas and Louisiana; and in many other eastern counties. The subset of area-source VOC emissions is mapped in Figure 3-7; the major component in this category is emissions from vehicles.

3.4.1.4 Geographic Distribution of Manmade Emissions of Nitrogen Oxides. An overall picture of the nationwide distribution of NO_x emissions can be obtained from the maps of the United States reproduced in Figures 3-8 and 3-9. Figure 3-8 shows total NO_x emissions by United States counties as compiled in the National Emissions Data System (NEDS) file of February 1978 (U.S. Environmental Protection Agency, 1978). Regions of high source emissions are evident near populous and industrial areas. Figure 3-9 shows the subset of area-source emissions, which is dominated by emissions from vehicles.

3.4.1.5 Profiles of Emissions of Volatile Organic Compounds. Hundreds of volatile organic compounds have been detected in the ambient air of urban areas, most of which can participate in photochemical reactions. Some limitations on the accuracy of emission inventories for these hydrocarbons and other VOC were mentioned in section 3.4.1. Additional factors such as atmospheric chemical reactions, variations in meteorological dispersion, and varying three-dimensional emission source distributions result in complex relationships between even comprehensive and accurate emission inventories and actual ambient air concentrations of VOCs.

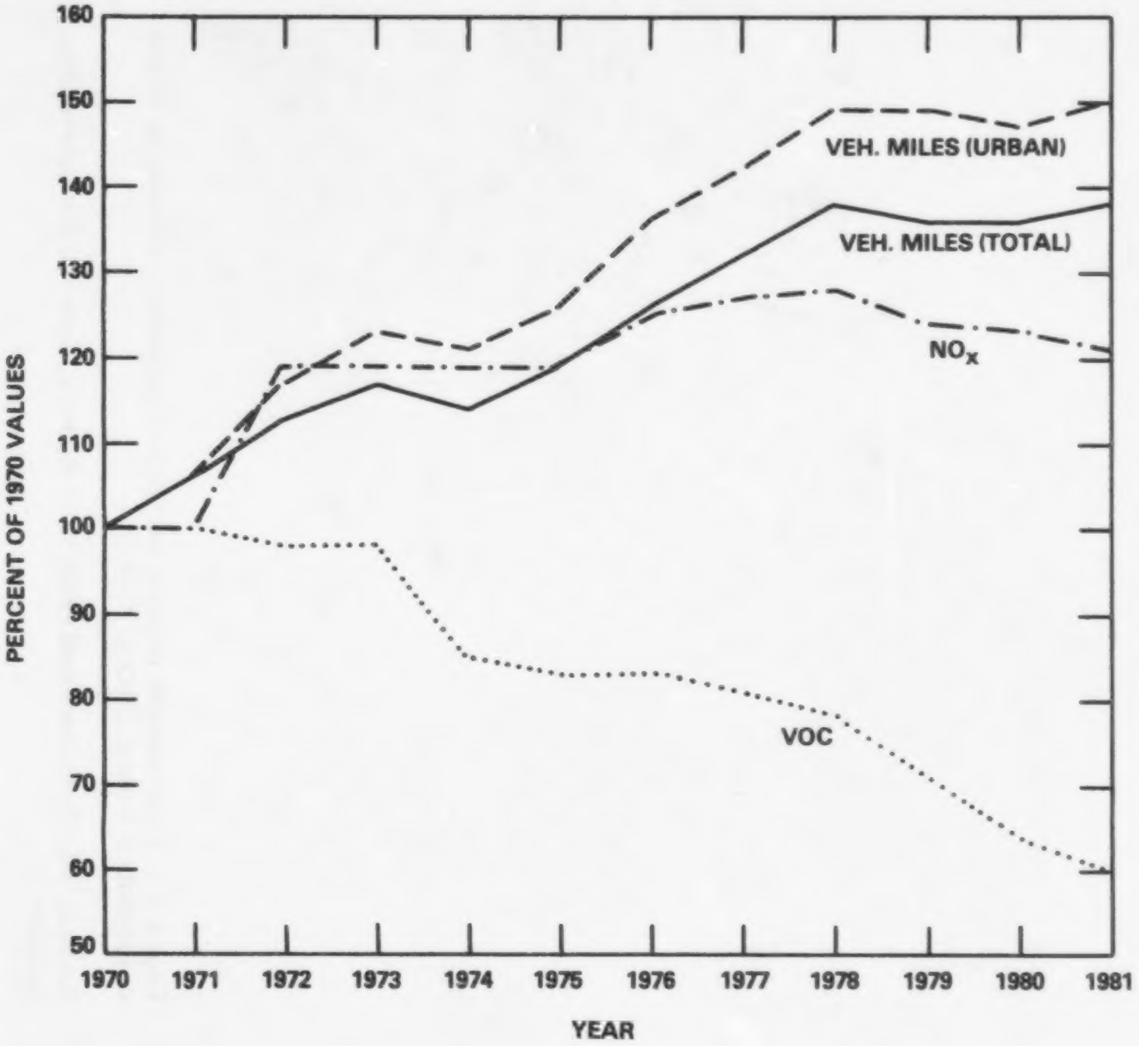

Figure 3-5. Comparative trends in mobile source emissions of nitrogen oxides (NO_X) and volatile organic compounds (VOC) versus vehicle miles traveled, 1970 through 1981.

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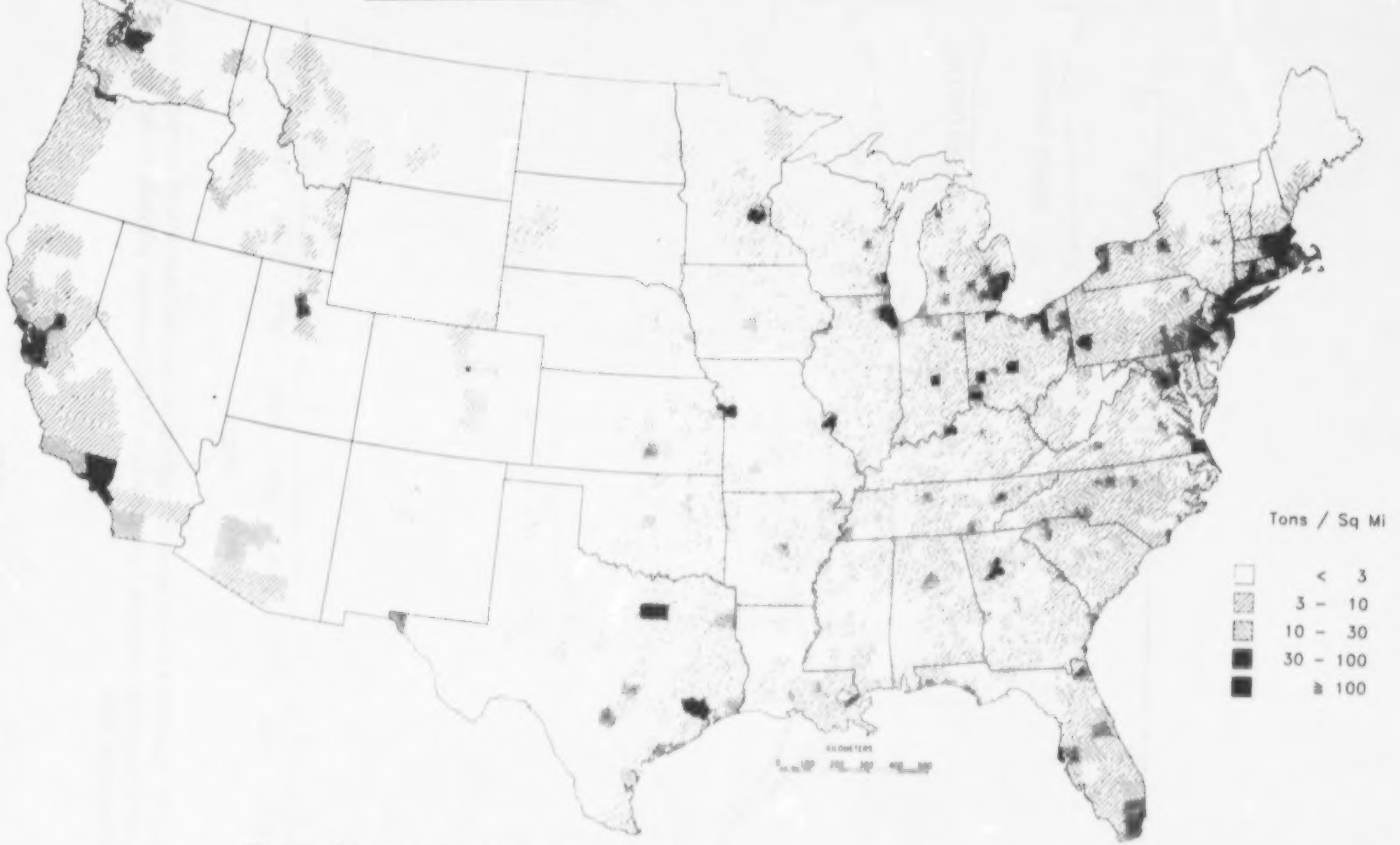
Tons / Sq Mi
□ < 3
▨ 3 – 10
▨ 10 – 30
■ 30 – 100
■ ≥ 100
KILOMETERS
0 100 200 300 400 500

Figure 3-6. Total volatile organic compound emissions by county in the coterminous United States, 1978.

SASD OAQPS 01 Apr 1983

Source: U.S. Environmental Protection Agency, National Emissions Data System.

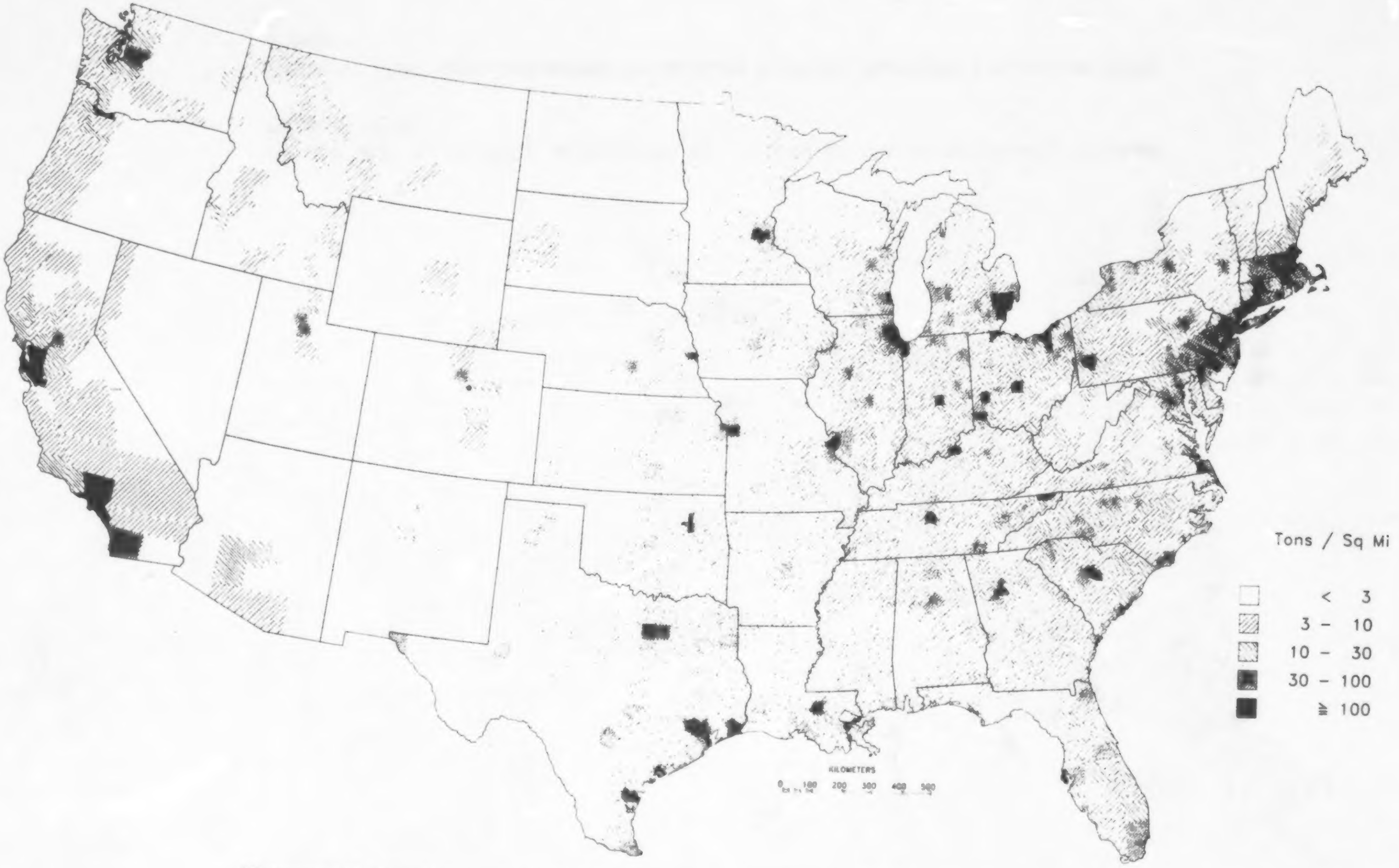
Tons / Sq Mi
< 3
3 - 10
10 - 30
30 - 100
≧ 100
KILOMETERS
0 100 200 300 400 500

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Figure 3-7. Area source volatile organic compound emissions by county in the coterminous United States, 1978.

Source: U.S. Environmental Protection Agency, National Emissions Data System.

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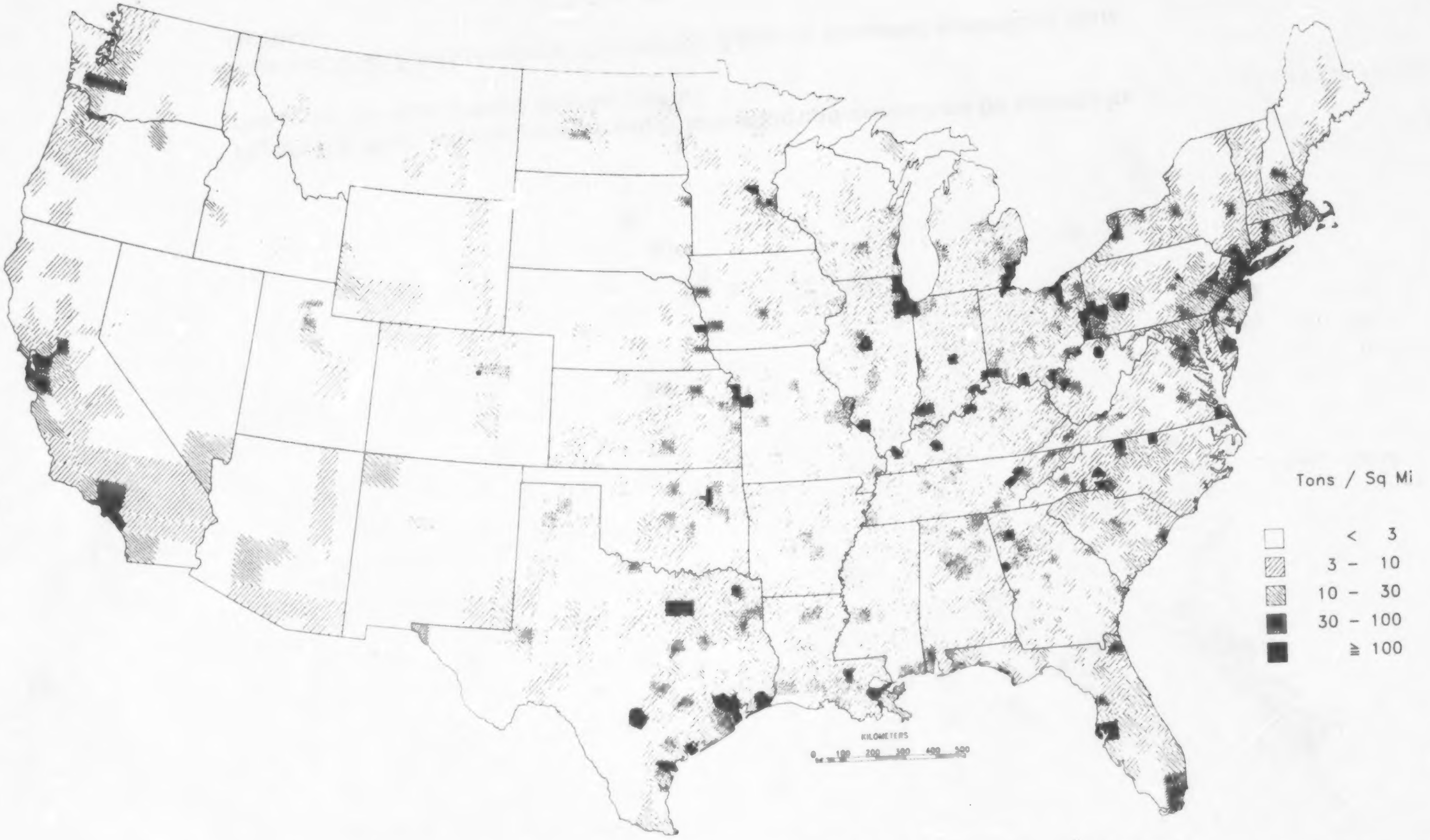
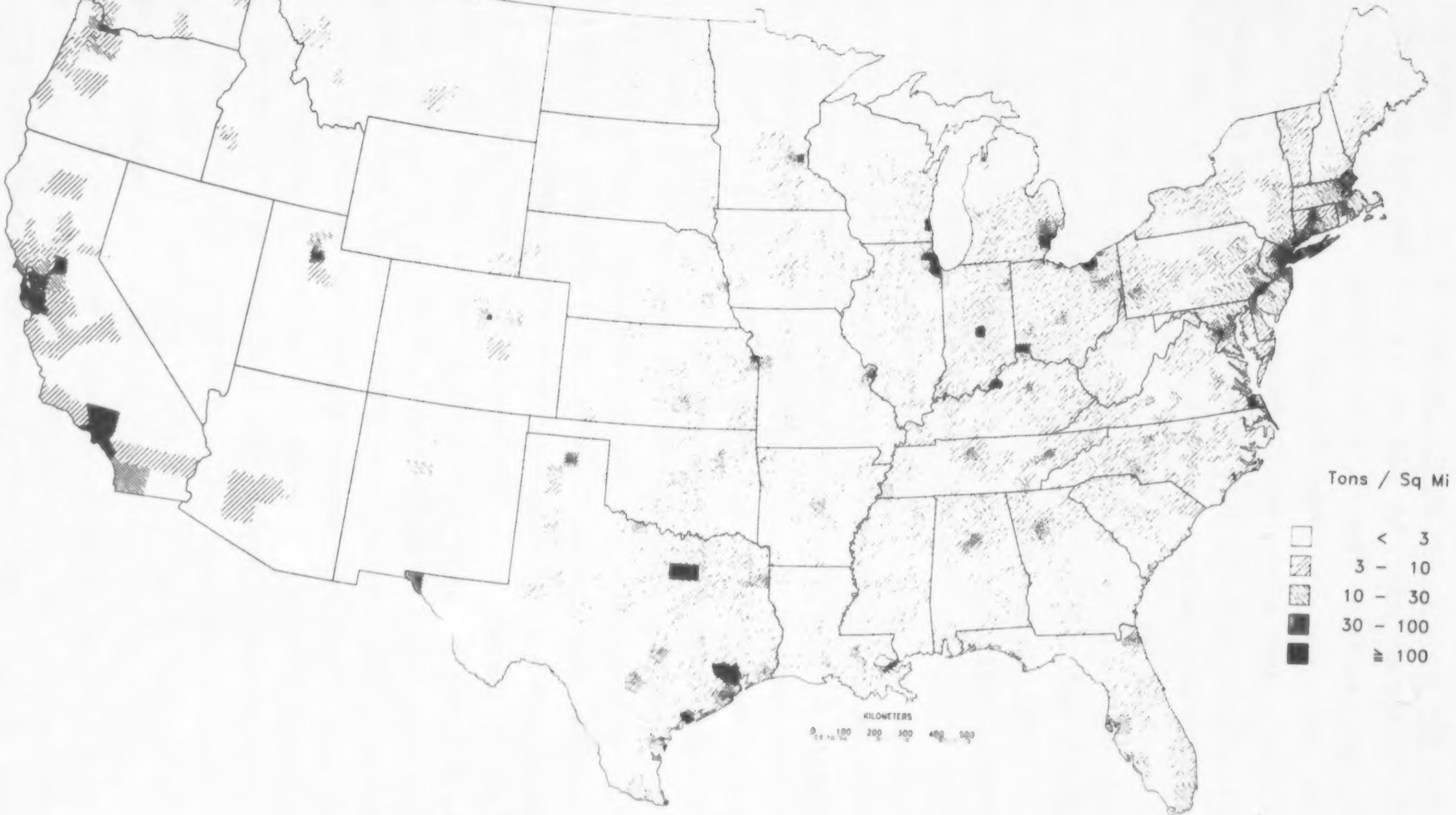

Tons / Sq Mi
☐ < 3
▨ 3 - 10
▨ 10 - 30
■ 30 - 100
■ ≧ 100
KILOMETERS
0 100 200 300 400 500

SASD OAQPS 01 Apr 1983

Figure 3-8. Total NO_X emissions by county in the coterminous United States, 1978.

Source: U.S. Environmental Protection Agency, National Emissions Data System.


Tons / Sq Mi
< 3
3 - 10
10 - 30
30 - 100
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KILOMETERS
0 100 200 300 400 500

SASD OAQPS 01 Apr 1983

Figure 3-9. Area source NO_x emissions by county in the coterminous United States, 1978.

Source: U.S. Environmental Protection Agency, National Emissions Data Systems.

3.4.1.5.1 Ambient air profiles and source reconciliation. The comparison of chemical species in ambient air with species actually emitted by respective sources is often referred to as "source reconciliation." Source reconciliation techniques can be used along with dispersion and other models to help validate emission inventories. More often, source reconciliation techniques are used to identify the relative contributions of various sources to the observed ambient pollutant mixture, based on the characteristic emission profiles of individual source categories.

Composition profiles of hydrocarbons (HC) in ambient air have been reported and compared with emission profiles of known sources by a number of investigators (Neligan, 1962; Stephens and Burleson, 1969; Lonneman et al., 1974; Siddiqi and Worley, 1977; Kopczynski et al., 1975; Mayrsohn and Crabtree, 1975; Mayrsohn et al., 1977; Crabtree and Mayrsohn, 1977; and Seila, 1979). For example, Lonneman et al. (1974) measured ratios of ethylene, isobutane, n-butane, isopentane, and n-pentane to the nonreactive compound, acetylene, which is considered a tracer of auto emissions. Subsequent investigations by other authors (Kopczynski et al., 1975) confirmed these as characteristic of automotive sources and estimated, for example, that, overall, fewer than 50 percent of the alkanes and aromatic hydrocarbons in ambient air in St. Louis were related to automotive emissions; whereas most of the alkenes in the evening and early morning hours were automotive-related. Using a multivariate regression technique, Mayrsohn and Crabtree (1975) estimated that the sources of the average distribution of nonmethane hydrocarbons (NMHC) in Los Angeles were as follows: 47 percent automotive exhaust; 31 percent gasoline; 8 percent commercial natural gas; and 14 percent geogenic natural gas. Thus, automotive-related sources contributed about 78 percent of the C_2 to C_{10} NMHC in 1973 in Los Angeles. These investigators subsequently extended their analysis to eight sampling sites between Los Angeles and Palm Springs and obtained similar results: automotive exhaust, 53 percent; gasoline, 12 percent; gasoline vapor, 10 percent; commercial natural gas, 5 percent; geogenic natural gas, 19 percent; and liquified petroleum gas, 1 percent. In a similar type of study in Houston, Texas, Siddiqi and Worley (1977) concluded that both automotive and industrial sources were significant contributors to ambient air NMHC in the Houston area, but that in downtown Houston, automotive sources dominated. There is some question, however, regarding their methods (Lonneman and Bufalini; 1978) and their interpretation (Crabtree and Mayrsohn, 1977). In a state forest about 38 miles north of Houston, Seila (1979) found that automotive sources accounted for 35 percent of the NMHC burden. Of the nonautomotive NMHC sources, the author concluded that 41 percent originated in Houston and 59 percent from sources north of Houston. Biogenic NMHC emissions were reported as accounting for only 2 percent of the NMHC loading. (Emissions of NMHC from vegetation will be discussed in section 3.4.2.)

3.4.1.5.2 Stationary sources of volatile organic compounds. The source category contributing the largest percentage of VOC emissions in 1982, 39 percent, is Industrial Processes (Table 3-9). The category consists almost entirely of point sources. The composition of these emissions varies widely, depending on the process or product and the use of emission reduction equipment and operating practices.

The second largest VOC source category, Transportation, accounting for 33.5 percent of the annual total in 1982, is discussed in the section below on mobile sources.

The third largest VOC source category, Miscellaneous, accounts for 13.2 percent of the annual total, over half of which consists of the subcategory, Miscellaneous Organic Solvents. These emissions generally qualify as area-source emissions. One group of solvents is widely used in domestic products such as furniture polish, shoe polish, shaving soap, perfumes, cosmetics, shampoo, hair spray, hand lotion, rubbing alcohol, and nail polish remover. The predominant compounds emitted are isopropyl alcohol and ethyl alcohol (Bucon et al., 1978).

3.4.1.5.3 Mobile sources of volatile organic compounds. Emissions of volatile organic compounds from the production and marketing of gasolines and motor oils are classed as stationary source emissions and are included in the 1.5 tg/year of VOCs emitted by the petroleum refining industry (Table 3-9). Following their sale to vehicle owners, these products generate some 7.7 tg/year of mobile source VOC emissions.

Although a significant portion of mobile source VOC emissions arises from additional evaporation, the most conspicuous mobile source emissions are the combustion products. Black et al. (1980) reported emission factors for over 60 individual hydrocarbons in both tailpipe and evaporative emissions of four passenger cars: a 1963 Chevrolet (model unspecified), a 1977 Mustang, a 1978 Monarch, and a 1979 LTD-II. The vehicle tests involved four gasoline fuels of varying composition. The four passenger cars for which emission data were

TABLE 3-9. NATIONAL ESTIMATES OF VOLATILE ORGANIC COMPOUND EMISSIONS, 1982

Source category	Weight emitted, tg/yr	Percent
Transportation		
Highway vehicles	(4.8)	
Aircraft	(0.2)	
Railroads	(0.2)	
Vessels	(0.4)	
Other off-highway vehicles	(0.5)	
Transportation: total	6.1	33.5
Stationary source fuel combustion		
Electric utilities	(0.0)	
Industrial	(0.1)	
Commercial-institutional	(0.0)	
Residential	(1.9)	
Fuel combustion: total	2.0	11.0
Industrial processes		
Chemicals	(1.8)	
Petroleum (crude and products)	(1.4)	
Oil and gas	(1.4)	
Industrial solvent use	(2.4)	
Other	(0.1)	
Industrial: total	7.1	39.0
Solid waste disposal		
Incineration	(0.3)	
Open burning	(0.3)	
Solid waste: total	0.6	3.3
Miscellaneous		
Forest fires	(0.8)	
Other burning	(0.1)	
Miscellaneous organic solvent	(1.5)	
Miscellaneous: total	2.4	13.2
Total	18.2	100.0

Source: U.S. Environmental Protection Agency (1983).

given by Black et al. (1980) represent a wide range of exhaust and evaporative emission control configurations. The authors concluded that evaporative emissions constituted a significant fraction (one-third to one-half) of total hydrocarbon emissions from all of the tested vehicles. Evaporative hydrocarbon emissions were relatively more abundant in alkanes than the tailpipe emissions. Uncombusted fuel was responsible for most of the aggregate hydrocarbon emissions above carbon number 4; combustion products dominated below carbon number 4. (This report presents detailed emission data, to which the reader is referred.) Generally, catalytic tailpipe control systems were more effective in reducing the amount of unsaturated than saturated hydrocarbon emissions. Evaporative control devices theoretically should control the more volatile compounds (generally $\leq C_4$), but in this instance the impact of the devices on the composition of emissions was not clear.

Table 3-10 gives hydrocarbon exhaust emission factors (in g/mi) for gasoline-powered, light-duty vehicles (excluding California and high-altitude models), for model years 1968 through 1980 and by calendar year of operation. The effects of the age of the vehicle and of control devices are apparent. (Note the large drop in emissions with the 1975 model year when catalytic converters were first installed). The composite crankcase and evaporative hydrocarbon emission rate for these vehicles declined from 2.53 g/mi in 1968 through 1970 to 0.15 g/mi in 1980 (Fisher, 1980).

The average composition of gasoline vapor, determined from weighted averages of gasoline blending stocks and vapor pressures of respective compounds, consists primarily of alkanes: n-butane (38.1 vol %), isopentane (22.9 vol %), n-pentane (7.0 vol %), and isobutane (5.2 vol %). The remaining individual alkanes and the collective alkenes and aromatics each account for less than 5 percent by volume of the evaporative emissions from gasoline (PEDCo, 1978). It should be noted that various gasoline blends from about six different blending stocks are used to tailor gasoline characteristics to suit differing climatic regions of the United States. Evaporative emissions from diesel vehicles are negligible because of low fuel volatility (Linnel and Scott, 1962; McKee et al., 1962). Exhaust emissions from gasoline-fueled vehicles typically contain fuel components and low-molecular-weight hydrocarbons that are not present in the fuel. The predominant hydrocarbons in automobile exhaust, as reported in three separate studies, are shown in Table 3-11.

TABLE 3-10. HYDROCARBON EXHAUST EMISSION FACTORS[a] FOR LIGHT-DUTY, GASOLINE-POWERED VEHICLES FOR ALL AREAS EXCEPT CALIFORNIA AND HIGH-ALTITUDE (g/mi[b])

Model Year	July, calendar year of operation										
	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980
1968	4.3	5.0	5.7	6.3	6.9	7.4	7.9	8.3	8.7	9.1	9.4
1969	3.5	4.3	5.0	5.7	6.3	6.9	7.4	7.9	8.3	8.7	9.1
1970	2.7	3.5	4.3	5.0	5.7	6.3	6.9	7.4	7.9	8.3	8.7
1971		2.7	3.5	4.3	5.0	5.7	6.3	6.9	7.4	7.9	8.3
1972			2.7	3.5	4.3	5.0	5.7	6.3	6.9	7.4	7.9
1973				2.7	3.5	4.3	5.0	5.7	6.3	6.9	7.4
1974					2.7	3.5	4.3	5.0	5.7	6.3	6.9
1975						1.3	1.6	1.9	2.2	2.5	2.8
1976							1.3	1.6	1.9	2.2	2.5
1977								1.3	1.6	1.9	2.2
1978									1.3	1.6	1.9
1979										1.3	1.6
1980											0.3

[a] Emission factors for vehicles through model year 1975 and through calendar year 1975 are based on actual surveillance tests of in-use vehicles. Post-1975 calendar year factors for all model-year vehicles are projected. Deterioration factors used are: pre-1968, 0.58; 1968-1974, 0.53; 1975-1979, 0.23; and ≥ 1980, 0.23--all in g/mi per 10,000 miles of travel.

[b] To convert g/mi to g/km divide g/mi by 1.609.

Source: Fisher (1980).

TABLE 3-11. PREDOMINANT HYDROCARBONS IN EXHAUST EMISSIONS FROM GASOLINE-FUELED AUTOS

Hydrocarbon (HC)	Fraction of total HC, vol %		
	62-Car survey	15-Fuel study	Engine-variable study[a]
Methane[b]	16.7	18	13.8
Ethylene[b]	14.5	17	19.0
Acetylene[b]	14.1	12	7.8
Propylene[b]	6.3	7	9.1
n-Butane	5.3	4	2.3
Isopentane	3.7	4	2.4
Toluene	3.1	5	7.9
Benzene[b]	2.4	NA[c]	NA
n-Pentane	2.5	NA	NA
m- + p-Xylene	1.9	NA	2.5
1-Butene	1.8	3[d]	6.0[d]
Ethane[b]	1.8	NA	2.3
2-Methylpentane	1.5	NA	NA
n-Hexane	1.2	NA	NA
Isooctane	1.0	NA	NA
All others	22.0	30	26.9

[a] Variables were air:fuel ratio and spark timing.

[b] Combustion products.

[c] NA = Data not available.

[d] Includes isobutylene.

Source: National Academy of Sciences, 1976.

The use of catalytic converters has had a pronounced effect not only on the amount of hydrocarbons emitted from automobiles but also on the actual species of hydrocarbons. In general, oxidation catalysts have resulted in an increase in the percentage of the less reactive alkanes, especially methane, and a decrease in the percentage of alkenes and acetylene. Typically, exhaust from a catalyst-equipped automobile contains about 62 percent alkanes, 17 percent aromatics, 18 percent alkenes, and 3 percent acetylene. This may be compared with the corresponding typical values for automobiles without converters: 40, 24, 26, and 11 percent, respectively. Methane levels generally range from about 10 to 30 percent (Black and Bradow, 1975; Black, 1977). Exhaust gases from gasoline-fueled vehicles also contain nonhydrocarbon organic compounds such as aldehydes, ketones, ethers, esters, acids, and phenols, amounting to as much as one-tenth of the total hydrocarbon content.

Factors other than gasoline composition influence the composition of exhaust. These include driving patterns, the specific configuration of emission control devices, ambient temperature and humidity, and, of course, individual automobile parameters such as tuning, make, and model year. Fuel additives can also influence emissions. For example, in one study, tetraethyl lead increased hydrocarbon emissions by about 5 percent but did not change the type of emissions (Leihkanen and Beckman, 1971).

Emissions from diesel automobiles are the subject of two recent papers (Black and High, 1979; Gibbs et al., 1983). Black and High (1979) described the complexities of accounting for both the gaseous and the condensed or particle-bound hydrocarbons in the cooling exhaust stream on its way through the exhaust system. They reported total hydrocarbon (THC) emissions of 0.29, 0.35, and 0.45 g/mi from a turbo-Rabbit, a Nissan-Datsun, and an Oldsmobile, respectively. From 15 to 40 percent of these hydrocarbons were associated with particles by the time the exhaust stream exited the tailpipe. Gibbs et al. (1983) have reported THC emissions from 19 in-use diesel automobiles, representing 1977 to 1979 model years, that were tested periodically over a 28-month period. Emissions of THC at the end of the period ranged from 0.17 to 0.88 g/mi for individual vehicles and averaged 0.65 g/mi. It should be noted here that the population of diesel-powered passenger cars is not growing as rapidly as was once expected. Sales of diesel-powered cars peaked at 6 percent for 1981 models and dropped to less than 3 percent by 1983 (Automotive News, 1982a,b,; 1983a,b,c).

Dietzman et al. (1980, 1981) recently reported on emissions from both gasoline- and diesel-powered trucks, using the chassis version of the 1983 transient heavy-duty engine test procedure. This procedure permits a variety of comparisons between emissions from gasoline and from diesel engines. Hydrocarbon emission rates are slightly higher when minimum quality DF-2 fuel is used with the three 4-stroke engines tested. No differences were observed with the 2-stroke (DD 8V-71) engine.

A summary of both exhaust and evaporative emission characteristics of a variety of fuel types is presented in Table 3-12 (Tilton and Bruce, 1981).

3.4.1.6 Profiles of Emissions of Nitrogen Oxides. Fuel combustion is the dominant source of NO_x emissions nationally. Stationary sources contribute 51.8 percent and mobile sources contribute 43.8 percent (1981 estimates, see Table 3-13). In contrast to their contributions to VOC emissions (Table 3-9), industrial process sources contribute only about 3 percent to the national total NO_x emissions.

Table 3-14 documents NO/NO_x ratios in emissions from a variety of source types. Nitric oxide (NO) is the dominant oxide of nitrogen emitted by most sources; NO_2 generally comprises less than 10 percent of the total NO_x emissions. Note, however, that NO_2 forms upwards of 30 to 50 percent of the total NO_x emissions from certain diesel and jet turbine engines under specific load conditions. Tail gas from nitric acid plants, if uncontrolled, may contain about 50 percent NO_2. The variations in NO/NO_x ratios by source type reported in this table may be significant in local situations, as, for example, in the immediate vicinity of a high-volume roadway carrying a significant number of diesel-powered vehicles.

The combustion process converts some nitrogen from both the combustion air and the fuel into nitrogen oxides. To date, the most cost-effective procedures for reducing NO_x emissions from stationary combustion sources involve modification of combustion conditions rather than denitrification of fuels or treatment of flue gases (Hall and Bowen, 1982).

The principal categories of stationary combustion sources are electric utility boilers, industrial boilers, and industrial process heaters.

Baseline NO_x emissions from electric utility boilers were reported by Bartok et al. (1971, cited in Hall and Bowen, 1982) as 994 ppm NO_x from coal-fired units; 589 ppm NO_x from gas-fired units; and 360 ppm NO_x from oil-fired units. Combustion modifications achieved reductions in gas- and oil-fired

TABLE 3-12. SUMMARY OF EMISSION CHARACTERISTICS FOR AUTOS FUELED BY GASOLINE, DIESEL, AND ALCOHOL-GASOLINE OR ETHER-GASOLINE BLENDS

Auto, control device, or fuel	Emission characteristics
Gasoline-fueled, uncontrolled	1. Exhaust emissions: about 40% paraffins; 24% aromatics; 26% olefins; 11% acetylene. 2. Main components of exhaust emissions: methane, ethane, acetylene, ethylene, propylene, C_4 olefins, toluene, benzene, *n*-butane, *n*-pentane, isopentane, xylene; aldehydes and some organic acids, ketones, phenols. 3. Evaporative emissions: 70% of carburetor emissions are light paraffins and olefins; 90% of fuel-tank emissions are light paraffins and olefins.
Gasoline-fueled, catalytic converters	1. Exhaust emissions: about 62% paraffins, 17% aromatics, 18% olefins, 3% acetylene. Methane is about 10 to 30% of exhaust emissions. 2. Catalysts preferentially oxidize unsaturated HC. 3. Lower reactivity per gram HC emissions than from uncontrolled gasoline-fueled. 4. Lower net HC emissions than from uncontrolled gasoline-fueled.
Lead additives in gasoline	1. Presence of TEL increased HC emissions. 2. Absence of TEL (or TML) necessitates higher aromaticity of gasoline to achieve higher octane ratings.
Ethanol-gasoline blends (relative to gasoline)	1. Decreased exhaust THC emissions. 2. Increased evaporative THC emissions. 3. Increased aggregate (exhaust plus evaporative) THC emissions. 4. Aldehydes in exhaust increased from noncatalyst cars; unchanged from cars with oxidation catalysts; increased from cars with TWC catalysts. 5. Increase in ethylene fron noncatalyst cars; no increase from cars with oxidation catalysts. 6. Increases in acetic acid with increasing alcohol content.
MTBE-gasoline blends (relative to gasoline)	1. Decreased exhaust THC emissions. 2. Increased evaporative THC emissions, but less than with alcohol-gasoline blends. 3. Aldehydes increased from cars with TWC catalysts; decreased from cars with oxidation catalysts.
Methanol-gasoline blends (relative to gasoline)	1. Emission rate of exhaust THC not appreciably changed; composition changed. 2. Higher methanol in exhaust. 3. Aldehydes in exhaust increased from noncatalyst cars; no significant change in aldehydes with TWC catalysts; higher aldehydes with oxidation catalysts.

TABLE 3-12. SUMMARY OF EMISSION CHARACTERISTICS FOR AUTO FUELED BY GASOLINE, DIESEL, AND ALCOHOL-GASOLINE OR ETHER-GASOLINE BLENDS (continued)

Auto, control device or fuel	Emission characteristics
	4. Decreases in exhaust NH_3, HCN, photochemical reactivity with increases in % alcohol. 5. Increases in exhaust formic acid with increases in % alcohol.
100% Methanol (relative to gasoline)	1. Higher cold-start HC emissions. 2. Significantly lower hot-start HC emissions. 3. Exhaust emissions: mainly methane, ethane, ethylene. 4. Significantly higher methanol and aldehyde emission (aldehydes reduced by increasing compression ratio or adding water to methanol).
Diesels (relative to gasoline)	1. Almost exclusively exhaust emissions. 2. Emissions: light, cracked HC, mainly methane, ethylene, acetylene, propylene; also aldehydes (C_1-C_6), including acrolein), and acetone. 3. Lower reactivity per gram HC emissions. 4. Lower net HC emissions. 5. Higher carbonyl emissions (aldehydes, ketones).

Note: HCN = hydrogen cyanide
NH_3 = ammonia
TEL = tetraethyl lead
THC = total hydrocarbon
TML = tetramethyl lead
TWC = three-way catalyst
MTBE = methyl tertiary butyl ether

Source: Tilton and Bruce (1981).

TABLE 3-13. NATIONAL ESTIMATES OF EMISSIONS OF NITROGEN OXIDES, 1982

Source category	Weight emitted, tg/yr	Percent
Transportation		
Highway vehicles	(7.8)	
Aircraft	(0.1)	
Railroads	(0.7)	
Vessels	(0.2)	
Other off-highway vehicles	(0.9)	
Transportation: total	9.7	48.0
Stationary source fuel combustion		
Electric utilities	(6.2)	
Industrial	(2.7)	
Commercial-institutional	(0.3)	
Residential	(0.4)	
Fuel combustion: total	9.6	47.5
Industrial processes		
Nitric acid	(0.1)	
Petroleum refining	(0.2)	
Other	(0.3)	
Industrial: total	0.6	3.0
Solid waste disposal: total	0.1	0.5
Miscellaneous: total	0.2	1.0
Total	20.2	100.0

Source: U.S. Environmental Protection Agency (1983).

TABLE 3-14. NO/NO_x RATIOS IN EMISSIONS FROM VARIOUS TYPES OF SOURCES

Source type	NO/NO_x	Reference
Uncontrolled tail-gas from nitric acid plants	~ 0.50	Gerstle and Peterson, 1966
Petroleum refinery heaters--using natural gas	0.93-1.00	Hunter et al., 1979
Linear ceramic tunnel kiln	0.90-1.00	
Rotary cement kilns	0.94-1.00	
Steel soaking pit-natural gas	0.97-0.99	
Wood/bark boiler	0.84-0.97	
Black liquor recovery boiler	0.91-1.00	
Carbon monoxide boiler	0.98-1.00	
Large 2-cycle internal combustion engine--natural gas	0.80-1.00	
Combined cycle gas turbine	0.83-0.99	
Gas turbine electrical generator--#2 fuel oil	0.55-1.00 (no load)-(full load)	Wasser, 1976
Industrial boilers (variety of fuels)	0.90-1.00	Cato et al., 1976
Diesel-powered passenger car--Nissan	0.77-0.91 (idle)-(50mph)	Braddock and Bradow, 1976
Diesel-powered passenger car--Peugeot 204d	0.46-0.99 (idle)-(50mph)	Springer and Stahman, 1977a
Diesel-powered passenger car--various Mercedes	0.88-1.00	
Diesel-powered truck and bus--various engines	0.73-0.98	Springer and Stahman, 1977b
Mobile vehicles internal gasoline combustion engine	0.99-1.00	Hilliard and Wheeler, 1979
Aircraft turbines (JT3D, TF30)	0.13-0.28 (idle[a]) 0.73-0.92 (takeoff and cruise)	Souza and Daley, 1978

[a] Earlier studies (Lozano et al., 1968; Chase and Hurn, 1970) did not report such high idle concentrations of NO_2.

Source: U.S. Environmental Protection Agency (1981).

units of up to 80 percent, but no more than 50 percent in coal-fired units. In subsequent tests with coal-fired units, reductions of up to 62 percent were achieved (Crawford et al., 1974, 1978; cited in Hall and Bowen, 1982). Since coal has a higher nitrogen content than oil or gas, this may be near the limit of reductions achievable through combustion modification.

Baseline NO_x emissions from the varied population of industrial boiler designs were found to be most dependent on fuel (Cato et al., 1974, 1976; cited in Hall and Bowen, 1982). Coal-fired units had the highest average NO_x emissions (475 ppm); oil the next highest (120 to 293 ppm, depending on fuel grade); and natural gas the lowest (139 ppm). Average reductions of 12 to 22 percent, with a maximum reduction of 75 percent, have been demonstrated using one or more combustion modification techniques. Results were quite variable, depending on boiler design.

Similarly, industrial process heaters are of diverse design and function, produce quite varied baseline NO_x emissions, and respond to adjustments in combustion conditions with mixed results (Hunter et al., 1978, 1979; cited in Hall and Bowen, 1982). Most units fired with natural gas, refinery gas, No. 6 oil, or wood produced NO_x concentrations in the range of 76 to 320 ppm. Cement kilns heated with natural gas produced some high levels, ranging from 90 to 2250 ppm NO_x. Emission reductions among the industrial process heaters studied ranged from nil to 69 percent.

As might be expected, modifying combustion conditions in stationary combustion units to reduce NO_x emissions sometimes caused concomitant increases in CO and particulate emissions. Overall efficiency was sometimes reduced, sometimes increased.

Emissions of NO_x from mobile sources, gasoline- and diesel-fueled vehicles are affected by a number of variables such as speed, load, and air:fuel ratio (AFR), as reported recently by Hilliard and Wheeler (1979). They concluded that gasoline engines show a maximum emission of NO_2 at "lean" AFRs of about 17:1; whereas diesel engines show a maximum emission at very lean AFRs of about 70:1 and at low speeds, under which conditions as much as 30 percent of the NO_x emissions may be NO_2. An active platinum oxidation catalyst increases the NO_2 in both engine types at a catalyst temperature of about 470°C, but CO levels above 1000 ppm in gasoline engine exhaust can negate the conversion to NO_2.

Gibbs et al. (1983) reported on NO_x emissions from a group of 19 in-use diesel automobiles representing the 1977 to 1979 model years. Vehicle mileage, both initial and accumulated, varied considerably, but over the 28-month test period the average accumulation was 35,000 miles per vehicle. Emissions of NO_x at the conclusion of the period (phase 3), using the Federal Test Procedure, ranged from 0.84 g/mi to 3.15 g/mi. The general trend with accumulating mileage ranged from no change to a 20 percent decrease in NO_x emissions.

Smith and Black (1980) reported on emissions from four gasoline-powered passenger cars equipped with three-way catalyst (TWC) control systems. These catalysts oxidize hydrocarbons and carbon monoxide to carbon dioxide and water as conventional oxidation catalysts do; and at the same time, reduce NO_x to nitrogen (N_2). Values for NO_x emissions ranged from 0.41 to 0.89 g/km (0.66 to 1.43 g/mi) for the 1978 Federal Test Procedure; from 0.50 to 1.14 g/km (0.80 to 1.84 g/mi) for the Congested Freeway Driving Schedule; from 0.49 to 1.05 g/km (0.79 to 1.69 g/mi) for the Highway Fuel Economy Driving Schedule (HFET); and from 0.41 to 0.93 g/km (0.66 to 1.50 g/mi) for the New York City Driving Schedule (NYCC). All vehicles met the standard for which they were designed.

Two other recent papers by Dietzmann et al. (1980, 1981) deal with NO_x emissions from heavy-duty gasoline and diesel trucks. Using several test fuels, the authors found NO_x emissions from diesel engines ranging from 10.86 g/km (17.47 g/mi) to as much as 26.35 g/km (42.40 g/mi) while the engines were operating on the 1983 transient cycle chassis test. In another test with engines using leaded gasoline, NO_x emissions ranged from 7.64 to 9.68 g/km (12.29 to 15.58 g/mi). Detailed NO_x emission rates from four heavy-duty diesel engines for a number of fuels showed no obvious trends regarding the effect of different fuels on NO_x emissions. Instead, differences ranging from 12 to 27 g/km (19.3 to 43.4 g/mi) were seen among types of engines (Dietzman et al., 1980, 1981).

Factors influencing seasonal variations in NO_x emissions from mobile sources include temperature (about a 35 percent decrease in emissions per vehicle mile with an ambient temperature increase from 20 to 90°F) (Ashby et al., 1974), and number of vehicle miles traveled (about 18 percent higher in summer than in winter, nationwide) (Federal Highway Administration, 1978). There are also differences between vehicle miles traveled in urban versus rural areas and among states in different regions of the country (Federal

Highway Administration, 1978). Seasonal variations in NO_x emissions from stationary sources are also expected since fossil-fueled power plants produce an estimated 15 percent more NO_x in the summer than in the spring (U.S. Department of Energy, 1978). Greater degrees of variation and different seasonal patterns have been reported for different regions of the country (California Board of Sanitation, 1966). Diurnal emission variations, notably those associated with motor vehicle traffic, are also important because of their potential impact upon ambient air quality.

3.4.2 Natural Sources and Emissions

3.4.2.1 Natural Sources and Emissions of Volatile Organic Compounds. This section presents information on hydrocarbon emissions from biogenic sources. Sampling of natural sources for determination of hydrocarbon emission rates necessitates the use of techniques far different from those used to sample emissions from manmade sources. Whereas the Agency has formulated guidelines for preparing inventories of manmade emissions (section 3.4.1), comparable guidelines for preparing inventories of natural emissions do not exist. Knowledge of natural emissions of hydrocarbons and other VOC is still sufficiently formative to require additional research. Consequently, this section, unlike the previous section, includes a discussion of techniques used by researchers to inventory natural (biogenic) hydrocarbon emissions. It also includes estimates of emission rates for individual species and for all species in certain areas as well as across the United States.

During the 1970's, studies conducted in several different laboratories established that monoterpenes, which were known or expected to be present in ambient forest atmospheres, were quite reactive both in photochemical processes and in ozonolysis reactions. These laboratory studies demonstrated that biogenic hydrocarbons will produce ozone when they are irradiated in the presence of oxides of nitrogen. It has also been established, however, that natural hydrocarbons are oxidized by ozone under normal atmospheric conditions. There have been recent as well as earlier reports that ascribe both an ozone-producing and an ozone-scavenging role to biogenic hydrocarbons (Arnts and Gay, 1979; Roberts et al., 1983). Although the actual atmospheric fate of natural hydrocarbons is currently not well understood (i.e., oxidation to gas phase and aerosol products), a good deal of progress has been made toward characterizing the identities and magnitude of biogenic hydrocarbon emissions. The purposes of this section of the document are to (1) provide a brief summary of the types of hydrocarbons emitted by natural processes; (2) describe the experimental methods utilized to measure emission rates; (3) discuss procedures employed for establishing natural hydrocarbon inventories; and (4) furnish a tabulation of reported biogenic hydrocarbon emission inventories. For detailed information, the reader is referred to several excellent review articles (Altshuller, 1983; Bufalini and Arnts, 1981; Dimitriades, 1981).

Geogenic hydrocarbon emissions--those emanating from natural gas seeps, volcanoes, and geothermal venting--will not be considered for two reasons. First, the majority of hydrocarbons emitted by geogenic sources are low-molecular-weight alkanes that react very slowly in photochemical systems in the atmosphere. Second, hydrocarbon emission rates from geogenic sources are poorly understood, such that reliable data for these sources are sparse. Consequently, the ensuing discussion will be concerned only with biogenic emissions from vegetation.

3.4.2.1.1 Biogenic VOC emissions. As part of the photosynthesis process, the leaves of plants produce sugars that are converted to starches for storage, to cellulose for structural growth, and to a variety of secondary compounds that participate in the normal metabolism of the plant. The production of isoprenoid compounds is a normal metabolic process in all green plants. To date, isoprene and the monoterpenes (section 3.2) are the only biogenic hydrocarbons identified as emissions from vegetation. These compounds are of interest to atmospheric scientists largely because they are volatile enough to be released under normal environmental conditions and because they have been shown to be potential ozone precursors.

Measurements by Sanadze and Dolidze (1962) and Rasmussen (1964) suggested that isoprene was emitted by plants. Subsequent work by Rasmussen (1970) and Evans et al. (1982) associated isoprene emissions with a variety of plant species. Monoterpenes are emitted by coniferous trees as well as by some deciduous types of vegetation. The commonly identified monoterpenes are α-pinene, β-pinene, camphene, Δ^3-carene, limonene, myrcene, and β-phellandrene. In addition, the oxygenated monoterpenes, 1,8-cineole and camphor, have been detected in some plant emission samples. As a general rule, coniferous trees emit primarily monoterpenes, and deciduous vegetation emits isoprene.

3.4.2.1.2 Biogenic emission rates. Biogenic emission rates have been determined almost exclusively by enclosure techniques. This procedure involves enclosing the entire plant or a portion of it, such as a branch of a tree, in a bag or chamber constructed of light, transparent material. If the chamber is operated in a static mode, a background sample is collected immediately after enclosure. Emissions are then allowed to accumulate for a measured period of time, after which an emission sample is withdrawn from the chamber. The branch or plant is removed from the chamber and the leafy portion that was enclosed is dried and weighed. The emission rate is calculated from the difference in concentration between the background and emission samples divided by the time and the weight of biomass. Emission rates are generally expressed in units of micrograms per gram dry biomass per hour [$\mu g\ (g_{dry\ biomass})^{-1} hr^{-1}$]. Enclosure chambers can also be operated in a dynamic mode, in which case the emission rate is obtained by multiplying the concentration of biogenic hydrocarbons eluted from the chamber by the air flow rate and dividing this product by the weight of dried biomass.

Tables 3-15 and 3-16 provide a summary of isoprene and monoterpene emission rates measured by the enclosure method. Because biogenic emission rates are temperature-dependent, the corresponding temperatures are also listed in the tables. A comparison of the two tables indicates that during the daytime isoprene emission rates are generally higher than those reported for monoterpenes. Isoprene emission rates range from 3 to 233 $\mu g\ g^{-1}\ hr^{-1}$ at 30°C, whereas monoterpene rates vary from less than 1 to 15 $\mu g\ g^{-1}\ hr^{-1}$ at 30°C. No emission rate information is included in these tables for agricultural crops. A few emission measurements have been made for corn, tobacco, forage crops, and pasture; however, the data base is too small to permit development of reliable emission rate estimates. The biogenic emission rates recorded for these crops were in the range of 0.5 to 2 $\mu g\ g^{-1}\ hr^{-1}$ (Lamb et al., 1983).

Besides temperature, biogenic emission rates are affected by other environmental factors. Rasmussen (1972) reported that emission rates varied with species, plant maturity, resin gland integrity, and leaf temperature. Dement et al. (1975) found that the emission rate of monoterpenes from Salvia mellifera (California Black Sage) is dependent on the vapor pressures of the terpenes, the humidity, and the amount of oil present on the surface of the leaf. These investigators also reported that the emission rate is not directly dependent on the photosynthetic activity or on the stomatal opening of the plant. This suggested that the release mechanism was physical and that the terpenes were volatilized from the surface of the leaf rather than from the inside.

TABLE 3-15. ISOPRENE EMISSION RATES

Species	Common name	Emission rate, $\mu g\ g^{-1}\ hr^{-1}$	Temp., °C	Reference
Robinia pseudoacacia	Locust	11	30	Winer et al. (1983)
Platanus occidentalis	Sycamore	21	28	Evans et al. (1982)
Platanus racemosa	Sycamore	11	30	Winer et al. (1983)
Salix nigra	Willow	19	28	Evans et al. (1982)
Salix babylonica	Willow	233	30	Evans et al. (1982)
Salix caroliniana	Willow	12	30	Zimmerman (1979)
Washingtonia filifera	Palm	11	30	Evans et al. (1982)
Phoenix dactylifera	Palm	15	30	Evans et al. (1982)
Populus tremuloides	Aspen	38	28	Evans et al. (1982)
Populus deltoides	Cottonwood	28	28	Evans et al. (1982)
Quercus borealis	Oak	15	28	Evans et al. (1982)
Quercus dumosa	Oak	35	30	Winer et al. (1983)
Quercus laurifolia	Oak	10	30	Zimmerman (1979)
Quercus nigra	Oak	24	30	Zimmerman (1979)
Quercus laevis	Oak	23	30	Zimmerman (1979)
Quercus virginiana	Oak	9	30	Zimmerman (1979)
Quercus incana	Oak	44	30	Zimmerman (1979)
Quercus myrtifolia	Oak	15	30	Zimmerman (1979)
Quercus phellos	Oak	31	30	Zimmerman (1979)
Quercus agrifolia	Oak	49	30	Winer et al. (1983)
Liquidambar styraciflua	Sweetgum	14	28	Evans et al. (1982)
Liquidambar styraciflua	Sweetgum	8	30	Zimmerman (1979)
Picea engelmannii	Spruce	12	28	Evans et al. (1982)
Picea sitchensis	Spruce	3	28	Evans et al. (1982)
Eucalytus globulus	Eucalyptus	44	28	Evans et al. (1982)

TABLE 3-16. MONOTERPENE EMISSION RATES

Species	Common name	Emission rate, $\mu g\ g^{-1}\ hr^{-1}$	Temp., °C	Reference
Pseudotsuga taxifolia	Douglas fir	15	30	Knoppel et al. (1982)
Pinus ponderosa	Pine	5	30	Knoppel et al. (1982)
Pinus ponderosa	Pine	4	30	Rasmussen (1972)
Pinus palustris	Pine	6	30	Zimmerman (1979)
Pinus clausa	Pine	11	30	Zimmerman (1979)
Pinus elliotti	Pine	6	28	Evans et al. (1982)
Pinus elliotti	Pine	3	30	Zimmerman (1979)
Pinus sylvestris	Pine	6	30	Knoppel et al. (1982)
Pinus taeda	Pine	1	30	Knoppel et al. (1982)
Pinus taeda	Pine	4	30	Arnts et al. (1978)
Pinus halepensis	Pine	0.6	30	Winer et al. (1983)
Pinus canariensus	Pine	2	30	Winer et al. (1983)
Pinus radiata	Pine	0.6	30	Winer et al. (1983)
Picea abies	Spruce	5	28	Evans et al. (1982)
Picea engelmannii	Spruce	3	28	Evans et al. (1982)
Picea sitchensis	Spruce	1	28	Evans et al. (1982)
Eucalyptus globulus	Eucalyptus	8	28	Evans et al. (1982)
Acer saccharum	Maple	2	28	Evans et al. (1982)

Tingey and his coworkers have conducted extensive studies into the effects of environmental conditions on emission rates. Live-oak seedlings were used to study the influence of temperature changes, water stress, light intensity, and CO_2 levels on isoprene emission rates (Tingey et al., 1981). Isoprene emissions decreased to near zero levels in the dark. Water stress did not alter the emission rate significantly and exposure to subambient CO_2 levels caused a small increase in isoprene emission rate. During daylight, temperature appears to be the main factor controlling isoprene emissions. Figure 3-10 shows a typical example of the relationship between ambient temperature and the emission rate of isoprene.

In contrast to isoprene, monoterpene emission rates do not appear to be influenced by light intensity. The emission rate of α-pinene as well as rates for four other monoterpenes emitted by slash pine were similar under various levels of light and darkness (Tingey et al., 1980). A log-linear increase in emission rates of monoterpenes with temperature was observed, however, in the slash pine studies.

Peterson and Tingey (1980) have used published data to model isoprene and monoterpene emission profiles through the diurnal cycle. The predicted emission rates, which are averages for several species, are shown in Figure 3-11. This figure illustrates the light-dependence of isoprene emissions and the minimal fluctuation expected in monoterpene rates.

There has been considerable discussion concerning the validity of emission rate data obtained by the bag enclosure technique. Confidence in this method has been limited primarily by uncertainties associated with isolating the vegetation in an artificial environment. Temperature, humidity, and possibly CO_2 concentration are likely to be different inside the enclosure. Also, emission rates will certainly increase if the vegetation inside the enclosure has suffered physical damage. Other questions, such as how representative emission rates are when measured from just one branch and whether emission rates are commensurate with ambient biogenic hydrocarbon concentrations, are difficult to answer.

Attempts to validate the bag enclosure method have focused on comparing enclosure emission estimates with those obtained by alternate procedures. Biogenic emission fluxes have been determined in hardwood and coniferous forests using micrometeorological gradient procedures and the enclosure method (Lamb et al., 1983). In the gradient studies, the flux of a particular biogenic

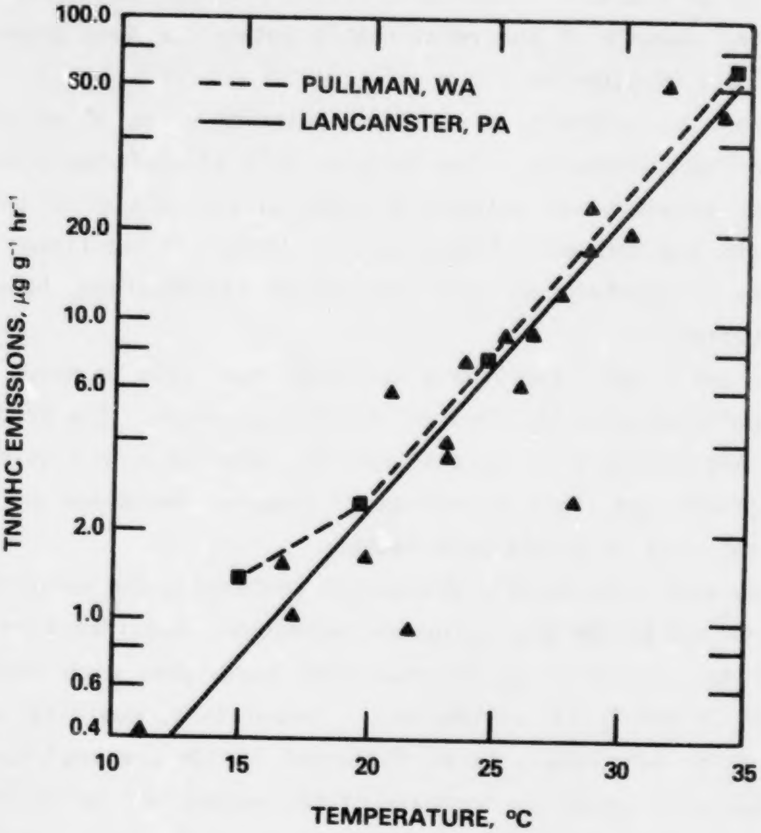

Figure 3-10. Total nonmethane hydrocarbon emission rate as a function of temperature for isoprene-emitting hardwoods at two sites.

Source: Flyckt et al. (1980)

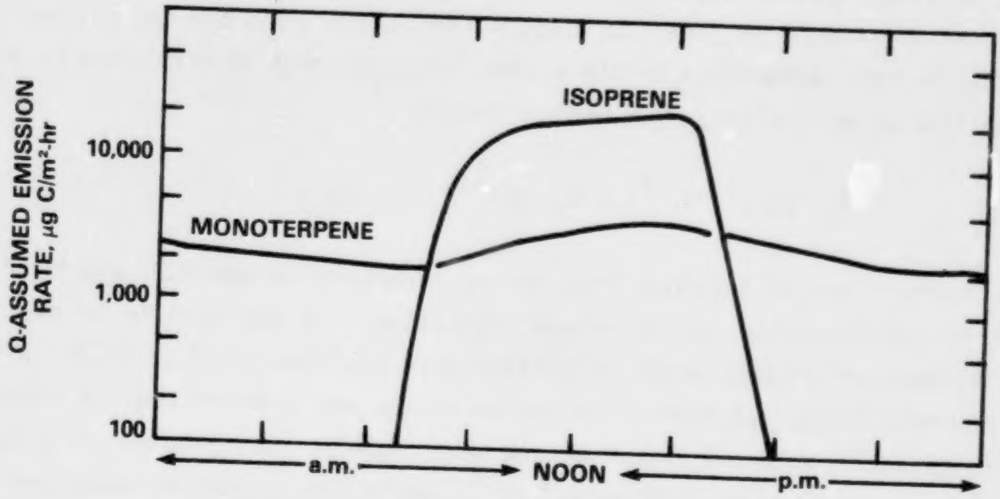

Figure 3-11. Estimated diurnal cycle of isoprene and monoterpene emission rates.

Source: Peterson and Tingey (1980).

hydrocarbon was determined from measurements of vertical eddy diffusivities and vertical hydrocarbon concentration profiles collected at respective levels along a tower extending above the forest canopy. Hydrocarbon flux was calculated on the basis of surface layer theory, where the flux is given as

$$F = K_z \, dc/dz \qquad (3\text{-}2)$$

and the vertical diffusivity, K_z, was obtained from vertical wind speed and temperature profiles. In order to compare the results from the two methods, the emission rates determined by the enclosure method must be converted to an emission flux by multiplying by a biomass factor:

$$E_r \; (\mu g \; g^{-1} \; hr^{-1}) \times B_f \; (g \; m^{-2}) = F \; (\mu g \; m^{-2} \; hr^{-1}) \qquad (3\text{-}3)$$

Biomass factors can be obtained from forest inventory information and from allometric relationships, which relate vegetation size and density to dry weight biomass per square meter of surface area (Sollins et al., 1973). At 30°C, isoprene fluxes obtained using the enclosure and gradient profile methods in a Pennsylvania hardwood forest agreed very closely. The gradient profile procedure gave a flux of 8,000 $\mu g \; m^{-2} \; hr^{-1}$, while the enclosure technique yielded 7,300 $\mu g \; m^{-2} \; hr^{-1}$ (Lamb et al., 1983). Good agreement has been reported, also, for α-pinene emission fluxes measured by a micrometeorological procedure and the enclosure method (Knoerr and Mowry, 1981).

Although the micrometeorological approach yields mass fluxes similar to the enclosure method, it, too, has certain limitations. The measurement of small vertical gradients above a forest canopy and the application of surface layer theory to non-ideal sites can lead to erroneous results. In many respects, the difficulties in measuring mass fluxes from a forest can be avoided by simulating the forest emissions with an inert tracer release and measuring ambient concentrations of the tracer and biogenic gases along downwind sample lines. The tracer approach does not require perturbation of the vegetation, nor does it rely upon precise gradient measurements. The only requirement is for an isolated source impacted minimally by upwind biogenic hydrocarbon contributions. Isoprene fluxes obtained using the tracer procedure in a central Washington oak grove compared well with flux estimates determined simultaneously with the enclosure technique (Allwine et al., 1983). Thus, it appears that if the bag enclosure procedure is applied properly representative biogenic emission rates will be acquired.

3.4.2.1.3 Biogenic emission inventories. The basic information required for development of a biogenic emission inventory is a knowledge of vegetation coverage, emission rates, and biomass factors. How these components are derived and utilized in the inventory process is illustrated through the following example.

A forested plot consisting of isoprene-emitting hardwoods is chosen for study. The emission rate of biogenic hydrocarbons is measured for representative types of vegetation within the plot. This is most easily accomplished using the enclosure method described previously. Sufficient data must be acquired so that the relationship between emission rate and temperature can be clearly defined. Once this has been accomplished, the size distribution and number of trees in the plot must be determined. Standard procedures that utilize random sampling techniques are employed for this type of forest survey. The information contained in the first four columns in Table 3-17 is derived directly from the forest survey. The next step in the inventory process is to determine the total leaf biomass for the study area, which is done by means of regression equations that relate biomass to a more easily measured tree parameter. Allometric equations ($y = ax^b$) that relate tree growth (biomass) to the proportions of trees have been developed by cutting down sample trees and subjecting them to intensive measurements. Figure 3-12 shows four allometric relationships that can be used to correlate biomass with tree diameter at breast height (DBH). Relationship number 4 was used together with the data in column number 4 of Table 3-17 to obtain biomass values for each tree species in this sample inventory (Table 3-17, column number 5). Multiplying the tree frequency by leaf biomass per tree gives a species total. Then, by summing the individual species totals, a biomass factor for the forest plot can be established. Finally, the biogenic hydrocarbon flux from the forest plot is obtained by multiplying this biomass factor by the appropriate emission rate value determined by the enclosure technique. An area-wide emission estimate can be obtained by multiplying the flux ($\mu g\ m^{-2}\ hr^{-1}$) by the area (m^2) of the forest plot.

Table 3-18 contains a listing of area-wide biogenic emission fluxes that have been reported for the United States and portions thereof. All of the emissions data contained in this table have been derived in a manner similar

TABLE 3-17. FOREST SURVEY DATA FOR ISOPRENE-EMITTING HARDWOODS

Species (Col. 1)	Canopy position (Col. 2)	Frequency, trees/ha (Col. 3)	Avg DBH, cm (Col. 4)	Leaf biomass, kg/tree (Col. 5)	Total biomass, kg/ha (Col. 6)
Black oak	Overstory	99.66	33.49	15.58	1552.70
	Understory	14.40	23.91	8.80	126.72
Chestnut oak	Overstory	41.53	31.08	13.73	570.21
	Understory	72.02	13.14	3.19	229.74
Black locust	Overstory	16.62	31.61	14.89	247.47
	Understory	14.40	13.32	3.62	46.94
Scarlet oak	Overstory	24.92	36.65	17.32	431.61
	Understory	0.0	0.0	0.0	0.0
White oak	Overstory	26.98	31.89	14.34	386.89
	Understory	33.59	19.11	6.02	202.20

Forest total = 3794 kg/ha
= 379 g/m^2

Source: Lamb et al. (1983)

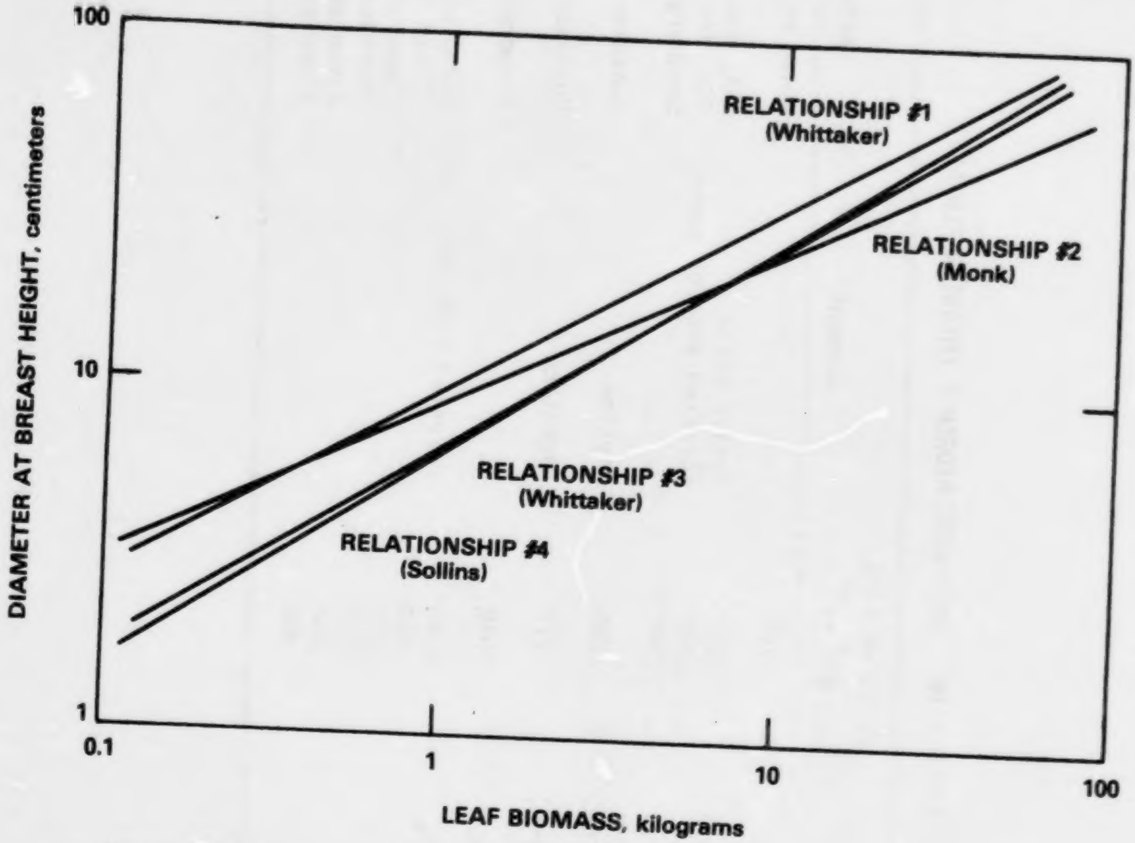

Figure 3-12. Comparison of four allometric relationships for determination of leaf biomass.

Source: Lamb et al. (1983).

TABLE 3-18. AREA-WIDE BIOGENIC EMISSION FLUXES

Location	Emission flux, µg m^{-2} hr^{-1}	Comment	Reference
South Coast Air Basin, California	$\leq$780	-	Winer et al. (1983)
Lake Tahoe, California	1950	Entire basin	JSA, Inc. (1978)
Lake Tahoe, California	2438	Forested area of basin	JSA, Inc. (1978)
San Francisco Bay Area, California	1388	-	Sandberg (1978)
San Francisco Bay Area, California	2265	Daytime	Hunsaker (1981)
San Francisco Bay Area, California	777	Nighttime	Hunsaker (1981)
Tampa/St. Petersburg, Florida	2540	-	Zimmerman (1979)
Southeastern Virginia	8890	Forested area only	Salop et al. (1983)
Pennsylvania	1660	-	Flyckt (1980)
Houston, Texas	1170	-	Zimmerman (1979)
United States	1712		Marchesani (1970)
United States	1099	-	Zimmerman (1977)
United States	884	-	Zimmerman (1978)

to that just described. Needless to say, accuracy of the estimate depends upon the size of the area for which the inventory has been prepared. Good biogenic emission estimates can be obtained for small forest plots that are well characterized in terms of emission rates, tree species, and biomass. When attempts are made, however, to inventory large areas such as the entire United States, much more uncertainty is introduced. As the size of the area increases, it becomes more difficult to select representative vegetation classes and to assign proper emission rates to them. Uncertainty in the assignment of biomass factors also increases as the size of the inventory base is expanded. In many cases, it is desirable to express emission estimates in terms of weight of biogenic emissions per day or per year. In these cases, it must be recognized that isoprene emissions are nearly zero at night and undoubtedly quite low in the winter when deciduous trees are without leaves. Also, since emission rates are temperature-dependent, variations in diurnal and seasonal temperatures must be considered. Many of these problems in preparing inventories have been discussed in detail (Altshuller, 1983; Zimmerman, 1981; Wells, 1981; Box, 1981; Dimitriades, 1981).

Considering all the variables, it is somewhat surprising that the area-wide emission fluxes listed in Table 3-18 show no more variation than they do. With the exception of the Southeastern Virginia area, which is a forested region with high biomass coverage, most values differ by less than a factor of three.

3.4.2.2 Natural Sources and Emissions of Nitrogen Oxides.

Natural emissions of nitrogen oxides (NO_x) originate from the oxidation of nitrogen gas by electrical discharge in the atmosphere, from the ammonification of organic nitrogen during biological decomposition, and from the oxidation of organic nitrogen during forest fires. Nitrogen fixation and electrical discharge are normal processes of the nitrogen cycle that convert inert nitrogen gas to biologically useful nitrate or ammonia.

The atmosphere, composed of 79 percent molecular nitrogen (N_2), is an important reservoir for nitrogenous compounds and provides a major link between terrestrial and aquatic ecosystems for the transport and transformation of gaseous and particulate forms of nitrogen oxides (NO_x). Figure 3-13 depicts the nitrogen cycle.

Nitrogen fixation is the conversion of inert nitrogen gas to biologically more usable forms, either by reduction to NH_4^+ or oxidation to NO_3^-. It has

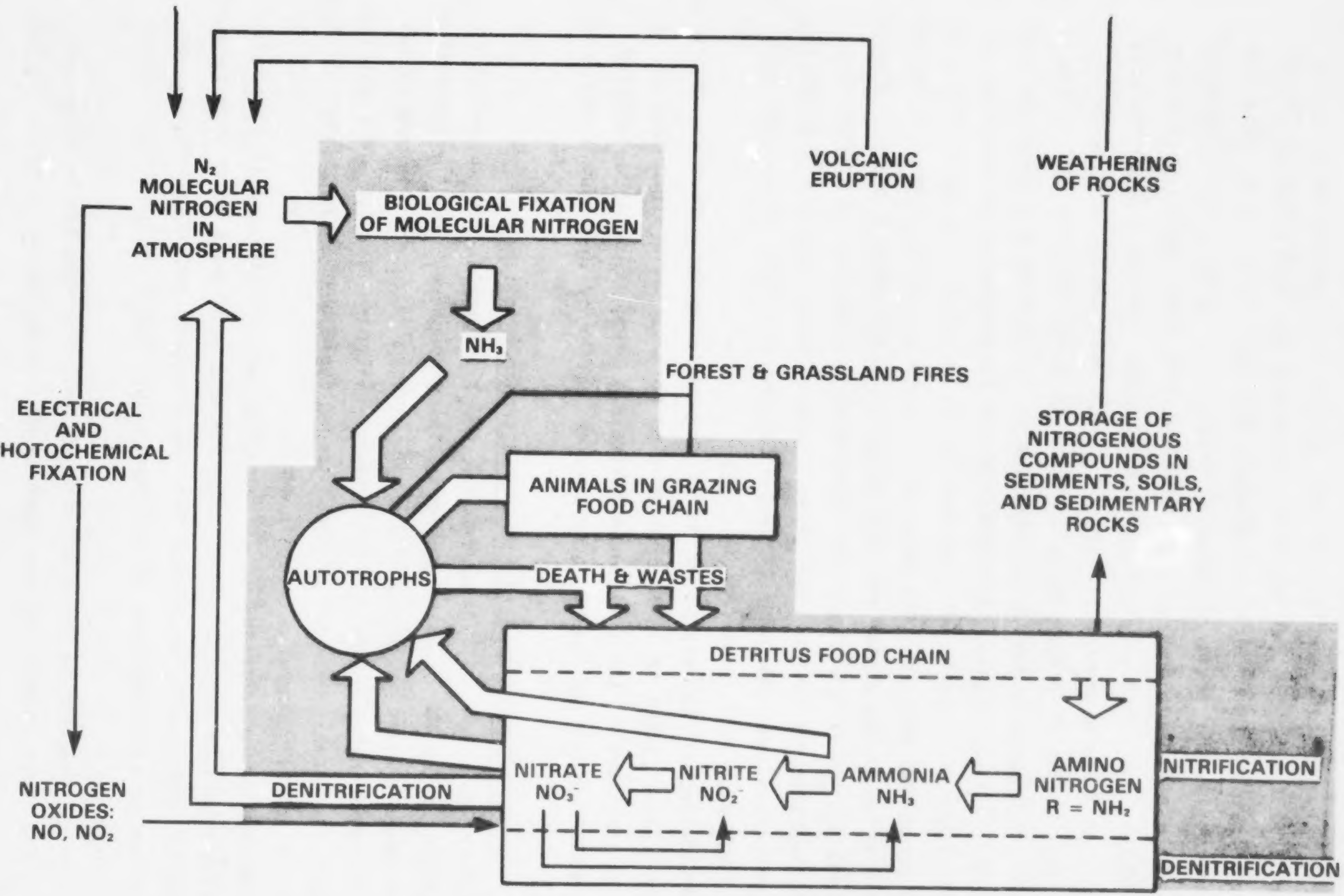
N_2
MOLECULAR NITROGEN IN ATMOSPHERE
BIOLOGICAL FIXATION OF MOLECULAR NITROGEN
VOLCANIC ERUPTION
WEATHERING OF ROCKS
NH_3
FOREST & GRASSLAND FIRES
ELECTRICAL AND PHOTOCHEMICAL FIXATION
STORAGE OF NITROGENOUS COMPOUNDS IN SEDIMENTS, SOILS, AND SEDIMENTARY ROCKS
ANIMALS IN GRAZING FOOD CHAIN
AUTOTROPHS
DEATH & WASTES
DETRITUS FOOD CHAIN
NITRIFICATION
NITRATE NO_3^-
NITRITE NO_2^-
AMMONIA NH_3
AMINO NITROGEN $R = NH_2$
NITROGEN OXIDES: NO, NO_2
DENITRIFICATION
DENITRIFICATION

Figure 3-13. The nitrogen cycle (organic phase shaded).

Source: U.S. Environmental Protection Agency (1982) been estimated that, on a global basis, nitrogen fixation in terrestrial ecosystems accounts for the production of 139 Tg of fixed nitrogen each year; leguminous plants account for 35 Tg of this total with the remainder being produced by free-living nitrogen-fixing microorganisms in forest and grasslands (Burns and Hardy, 1975). Estimates by other investigators differ considerably and are shown in Table 3-19. The amount of biologically fixed nitrogen actually released into the ambient air is unknown.

Lightning flashes in the troposphere can convert N_2 to NO via reaction with monatomic oxygen. Crutzen and Ehhalt (1977) estimated that from 8 to 40 Tg N are fixed by lightning each year. The work of Chameides et al. (1977) suggests that lightning is a significant source of NO_x. producing about 30 to 40 Tg NO_x-N per year. If this estimate is correct, lightning could account for as much as 50 percent of the total atmospheric NO_x on a global basis. Direct observations by Noxon (1976) have indicated that during a lightning storm ambient concentrations of NO_2 could possibly be enhanced by a factor of 500 over normal. The enhanced levels declined rapidly after passage of the storm. Liu et al. (1977) estimated NO_x production by lightning at 9 Tg per year.

Biological ammonification is an important process in the renewal of the limited supply of inorganic nitrogen. During the decomposition process, organic compounds, such as amino acids, are converted into NH_3 and ammonium ions. Volatilization of ammonia from soils may increase the atmospheric concentration of NO_x as NH_3 undergoes atmospheric transformations (National Academy of Sciences, 1978; Hill, 1971).

Total NO_x emissions to the atmosphere from terrestrial sources were reported by Soderlund and Svensson (1976) to be in the range of 8 to 25 Tg N per year. Soderlund and Svensson (1976) have hypothesized that a net flow of NO_x prevails from terrestrial to aquatic systems; losses of NO_x from aquatic systems to the atmosphere were considered insignificant.

Although 40 to 108 Tg NO_x-N per year has been estimated to be released from terrestrial sources to the atmosphere, the bulk is reabsorbed and only 8 to 25 Tg NO_x-N escapes to the troposphere (Robinson and Robbins, 1975). Hill (1971) reported that NO and NO_2 are absorbed, to some extent, from the atmosphere by plants. Using data obtained from the experiments of Marakov (1969), and those of Kim (1973), Soderlund and Svensson (1976) estimated that soil contributes to the atmosphere between 1 and 14 Tg N in the form of NO and NO_2;

TABLE 3-19. GLOBAL ESTIMATES OF NITROGEN TRANSFORMATION (Tg N/yr)

	Range of estimates	Reference[a]
Biological fixation $(N_2 \longrightarrow NH_4^+)$	54 to 270	1, 2, 3, 4, 5
Electrochemical fixation		
lightning $(N_2 \longrightarrow NO_x)$	10 to 40	2, 8
atmospheric $(N_2 \longrightarrow NO_2)$	14 to 20	2, 4
Biological denitrification		
$(NO_{3-} \longrightarrow N_2)$	96 to 190	2, 3
$(NO_3 \longrightarrow N_2O)$	20 to 340	2, 3, 4
combined	83 to 270	5, 6, 7
Industrial denitrification		
(Organic -N $\longrightarrow NO_x$)	14 to 19	2, 3, 4
(Other $\longrightarrow NO_x$)	30 to 36	2, 3, 5
Atmospheric denitrification $(NH_3 \longrightarrow NO_x)$	3 to 30	2, 3
Natural NO_x emissions (land and sea)	40 to 210	3, 4
NH_3 emissions to atmosphere from land and sea	110 to 850	2, 3, 4

[a] 1. Delwiche (1970).

2. Burns and Hardy (1975).

3. Soderlund and Svensson (1976).

4. Robinson and Robbins (1975).

5. Liu et al. (1977).

6. Sze and Rice (1976).

7. Council for Agricultural Science and Technology (1976).

8. Chameides et al. (1977).

losses from aquatic ecosystems to the atmosphere were considered by these authors to be minor. The principal source of gaseous NO_x in terrestrial systems is believed to be the decomposition of nitrates (Soderland and Svensson, 1976).

3.4.2.3 Local Natural Sources of NO_x. Since the ozone/oxidant-forming potential of natural sources of precursors depends to some degree upon their local distributions, it is worthwhile to examine local sources of NO_x. In this section, available estimates of emission rates of NO_x from fresh water, swamps, soil, and vegetation are presented.

The fate of nitrogen in fresh water has been reviewed by Keeney (1973) and by Brezonik (1973). Molecular nitrogen is the main product of denitrification, a biochemical process; NO (or N_2O) is seldom detected (Black and High, 1979). Brezonik (1973) concluded that denitrification did not appear to be a significant process in Florida lakes. In Smith Lake, Alaska, Goering and Dugdale (1966) failed to detect NO or N_2O, although N_2 as a product of denitrification was present. Under acid conditions resulting from high concentrations of polyphenolic substances such as tannins, lignins, and humic acid, the purely chemical reaction of nitrous acid with organic substances could result in a significant source of NO_x (Brezonik, 1973). Direct measurement of this as a possible source of emissions, however, appears to be lacking.

There is no direct evidence that plants emit any NO_x into the atmosphere, although they contain, and exchange with their local environment, significant quantities of nitrogen in various oxidation states. In addition, data are lacking on possible NO_x exchange from forest litter (Ratsch and Tingey, 1978).

Wijler and Delwiche (1954) identified NO as a product of denitrification processes in soil, although N_2 was the major initial product. At least two studies (Renner and Becker, 1970; Payne et al., 1971) have shown that NO is a specific product of the bacterial reduction of nitrate in soil; N_2O, however, is the terminal product of reduction in several bacterial strains. It may be expected, from the work of Cady and Bartholomew (1961) on N_2 production in soil, that NO production will increase as soil oxygen decreases. Under anoxic conditions, however, Cady and Bartholomew found that N_2O was reduced to NO. Bailey (1976) found that increases in soil temperature resulted in decreases in NO production.

In addition to biochemical processes, there is evidence that purely chemical reactions in the soil produce N_2 and NO_x under certain conditions (Delwiche and Bryan, 1976; Porter, 1971).

Stevenson et al. (1970) showed evidence that NO, N_2O, and N_2 could be produced by nitrosation of humic and fulvic acids, lignins, and aromatic substances at pH 6.0 and 7.0 in the absence of oxygen. Steen and Stojanovic (1971) found that NO was volatilized from a calcareous soil when high concentrations of urea were nitrified with concurrent accumulation of nitrite, and assumed that nitrosation between nitrous acid and organic matter was the main pathway by which NO was formed.

Wullstein and Gilmour (1964, 1966) reported that nitrite reacted with certain reduced transition metals in sterile, moderately acid systems to yield NO as a primary gaseous product.

Bremner and Nelson (1968) found that N_2 and NO_2 and small amounts of N_2O were formed when nitrite was added to neutral and acid soils. They suggested that the reactions between soil organic constituents and nitrite were responsible for the formation of N_2 and N_2O, while self-decomposition of HNO_2 was responsible for the formation of NO and NO_2. In steam-sterilized raw humus samples incubated with nitrite, NO was the predominant gaseous reaction product (Nommick and Thorin, 1971). Nelson and Bremner (1970a, 1970b) found that the formation of NO_2 by decomposition of nitrite in pH 5.0 solution was not promoted by organic or inorganic soil constituents and concluded that most of the NO_2 evolved was formed by self-decomposition of HNO_2. The amount of NO_2 formed was inversely related to soil pH, but pH had little effect on the amount of nitrite converted to nitrate. These findings led to the conclusion that the self-decomposition reaction of HNO_2 was best represented by the equation:

$$2HNO_2 \longrightarrow NO + NO_2 + H_2O \qquad (3\text{-}4)$$

Although more is known about the natural biological and chemical processes in the environment that produce emissions of nitrogen oxides than those that produce VOC, the problems with actually quantifying such emissions exceed the problems associated with quantifying natural emissions of VOC. As indicated in section 3.3, the limits of detection of methods for measuring nitrogen oxides are such that low-level measurements are often not reliable. Techniques for estimating NO_x emissions from such sources as lightning and biological processes are virtually nonexistent. In addition, scaling of emissions from such sources as bacterial nitrification and denitrification for use in preparing area-wide emission inventories is not possible. Thus, the emissions reported in this section should be taken as very gross approximations that serve to identify natural sources of NO_x and to present the relative magnitude of emissions from such sources.

3.5 REPRESENTATIVE CONCENTRATIONS OF OZONE PRECURSORS IN AMBIENT AIR

Nonmethane organic compounds (NMOC) and the oxides of nitrogen (NO_x) in the presence of sunlight react to form ozone and other photochemical oxidants. The reaction sequence is very complex, and therefore, it is difficult to establish dependable precursor-oxidant relationships. Factors such as absolute NMOC and NO_x concentrations, relative NMOC and NO_x concentrations, NMOC reactivity, and NO_x composition are known to effect the photochemical reactions that produce ozone and other oxidants in ambient atmospheres. The purpose of this section is to provide a summary of NMOC and NO_x concentrations recorded at various urban and nonurban locations in the United States.

3.5.1 Concentrations of Nonmethane Organics Compounds in Ambient Air

Automated total hydrocarbon analyzers have been employed for many years to measure ambient hydrocarbon concentrations. The accuracy of data obtained with these analyzers is questionable, however, because the methodology does not provide a direct measure of the nonmethane organic fraction. Rather, a total hydrocarbon value that includes methane is obtained and the methane concentration must be determined and substracted from the total. The indirect nature of the measurement, along with calibration difficulties, limits the usefulness of data obtained with total hydrocarbon analyzers. Consequently, nonmethane organic data obtained in this way will not be utilized in this discussion.

Gas chromatographic methods are now available that allow identification and quantification of individual hydrocarbon species. Total hydrocarbon concentrations are then derived by summation. This procedure works well for the "true" hydrocarbons, which contain only carbon and hydorgen atmos. Low-molecular-weight aldehydes are particularly troublesome and thus must be measured using alternate methods. Originally, ambient aldehyde concentrations were determined using chemical methods that were specific for formaldehyde and the combined series of aliphatic aldehydes. In more recent years, analytical methods employing liquid chromatography have been developed for measuring the concentration of individual aldehydes in ambient atmospheres.

For discussion purposes, the ambient NMOC data will be segregated in this section into two groups: (1) nonmethane hydrocarbons, and (2) oxygenated hydrocarbons. There is a fairly substantial data base for characterizing urban nonmethane hydrocarbon concentrations. Measurements of nonurban hydrocarbon levels, as well as both nonurban and urban oxygenated hydrocarbons, are much more limited. In the latter group, aldehydes have received the most attention. There is insufficient information available for establishing ambient air concentrations of other classes of oxygenated hydrocarbons such as alcohols, ketones, acids, and ethers.

3.5.1.1 Urban Nonmethane Hydrocarbon Concentrations. Most of the ambient air nonmethane hydrocarbon (NMHC) data have been obtained during the 6:00 to 9:00 a.m. time period. Since urban hydrocarbon emissions peak during that period of the day and atmospheric dispersion is limited, these concentrations generally reflect maximum diurnal levels. Table 3-20 lists the mean and range of NMHC concentrations recorded in a number of urban areas throughout the United States. For most urban areas included in the table, a mean NMHC value between 400 and 900 ppb C was observed. It is obvious, however, that Houston, Las Vegas, and Los Angeles exhibit mean values in excess of 1000 ppb C. The data in Table 3-20 are not meant to serve as a comparison of NMHC levels in various cities but rather are shown to indicate the mean and range of concentrations that have been reported. Comparisons are invalid because of major differences in sample numbers, site classifications, and seasonal sampling periods. It can be seen that the range of NMHC concentrations measured in some urban areas can vary by as much as two orders of magnitude. For example, the lowest and highest NMHC concentrations recorded in Milwaukee were 24 ppb C and 3116 ppb C, respectively. In many cases, the range of values reported in Table 3-20 might not reflect the true maximum and minimum concentrations that occur in a particular urban area. Most of the hydrocarbon sampling programs were of short duration (~1 month) and in some cases were not operated on a daily basis. For example, the relatively high mean values reported in Las Vegas are undoubtedly the result of the fact that ambient air samples were only analyzed for hydrocarbons on days when conditions were appropriate for oxidant formation. It is probably safe to assume, however, that NMHC levels during the 6:00 to 9:00 a.m. time period in major urban areas will usually exceed 50 ppb C but seldom surpass 10,000 ppb C.

The hydrocarbon composition of urban atmospheres is dominated by species in the C_2 - C_{10} molecular-weight range. The alkanes are most prominent, followed by aromatics and alkenes. Based on speciation data obtained in several urban areas, alkanes generally constitute 50 to 60 percent of the hydrocarbon burden, aromatics 20 to 30 percent, with alkenes and acetylene making up the remaining 5 to 15 percent (Sexton and Westberg, 1984). The alkane fraction is usually dominated by species in the C_4 - C_6 molecular-weight range: i-butane, n-butane, i-pentane, n-pentane, 2-methylpentane, 3-methylpentane, hexane, etc. Predominant aromatics include benzene, toluene, ethylbenzene, and the xylenes. Ethylene and propene are normally the most abundant alkenes, with lesser amounts of the isomeric occurring. Table 3-21 shows a typical example of the hydrocarbon composition recorded in urban atmospheres.

3.5.1.2 Nonurban Nonmethane Hydrocarbon Concentrations . Nonurban nonmethane hydrocarbon concentrations are generally one to two orders of magnitude lower than those measured in urban areas (Ferman, 1981; Sexton and Westberg, 1984). On an individual species basis, concentrations seldom exceed 10 ppb C; total hydrocarbon concentrations range up to ~150 ppb C, but usually fall in the range of about 5 to 100 ppb C. Alkanes comprise the bulk of species present, with ethane, propane, n-butane, i-pentane, and n-pentane most abundant. Ethylene and propene are occasionally reported at concentrations of 1 ppb C or less, and toluene is usually present at ~1 ppb C. Table 3-22 provides a summary of the range of hydrocarbon concentrations measured at various nonurban locations in the United States. Samples were carefully selected at most of the sites in order to guarantee their nonurban character. At the coastal and near-coastal sites, only those samples collected upwind of manmade sources (onshore advection) were included. The nonmethane hydrocarbon concentrations reported at coastal sites (Belfast, Benicia, Miami, and Houston) are definitely lower than those measured at most of the inland sites. It should be pointed out, however, that the numbers of samples measured for each of the nonurban locations listed in Table 3-22 is small. This, coupled with the fact that only a limited range of hydrocarbons were monitored in some cases, makes intersite comparisons tenuous at best.

In recent years there has been considerable interest in the ambient air concentrations of naturally emitted hydrocarbons. The species most often reported include isoprene, α-pinene, β-pinene, Δ-carene, and limonene. These species are generally reported only in nonurban hydrocarbon sampling programs.

TABLE 3-20. NONMETHANE HYDROCARBON CONCENTRATIONS MEASURED BETWEEN 6:00 and 9:00 a.m. IN VARIOUS UNITED STATES CITIES

City (Date)	Mean NMHC conc., ppb C	Range	Reference
Atlanta (1981)	491	113 to 1677	Westberg and Lamb (1983)
Baltimore (1980)	659	51 to 2798	Sexton and Westberg (1984)
Boston (1980)	569	83 to 4750	Sexton and Westberg (1984)
Cincinnati (1981)	840	260 to 1870	Holdren et al. (1982)
Houston (1976)	1414	356 to 16,350	Sexton and Westberg (1984)
Houston (1978)	1679	400 to 4500	Lonneman (1979)
Las Vegas (1980)	2506	689 to 4515	Naylor et al. (1981)
Las Vegas (1983)	2762	1835 to 4590	Naylor et al. (1984)
Los Angeles (1968)	3388	- - -	Lonneman (1977)
Los Angeles (1982)	2920	390 to 6430	Grosjean and Fung (1984)
Milwaukee (1981)	324	24 to 3116	Sexton and Westberg (1984)
Newark (1980)	732	89 to 6946	Sexton and Westberg (1984)
New York (1969)	830	- - -	Lonneman (1977)
Philadelphia (1979)	669	305 to 1710	Sexton and Westberg (1984)
St. Louis (1973)	817	- - -	Lonneman (1977)
Tulsa	426	103 to 3684	Eaton et al. (1979)
Washington, D.C. (1980)	671	210 to 2953	Sexton and Westberg (1984)

TABLE 3-21. HYDROCARBON COMPOSITION TYPICALLY MEASURED IN URBAN AREAS
(From sample collected in Milwaukee, 1981)

ppb C	Hydrocarbon	ppb C	Hydrocarbon
14.0	Ethane	4.5	2-Methylhexane
25.5	Ethylene	5.5	2,3-Dimethylpentane
16.0	Acetylene	8.0	3-Methylhexane
18.5	Propane	5.0	2,2,3-Trimethylpentane
9.5	Propene	8.0	*n*-Heptane
28.5	*i*-Butane	3.0	Methylcyclohexane
65.0	*n*-Butane	1.5	2,4-Dimethylhexane
2.0	1-Butene	1.5	2,3,4-Trimethylpentane
3.5	*i*-Butene	33.5	Toluene
3.5	*t*-2-Butene	--	2,3-Dimethylhexane
	c-2-Butene	2.5	2-Methylheptane
49.0	*i*-Pentane	2.5	3-Ethylhexane
24.0	*n*-Pentane	2.5	*n*-Octane
2.0	1-Pentene	--	Ethylcyclohexane
--	*t*-2-Pentene	6.5	Ethylbenzene
0.5	*c*-2-Pentene	18.5	*p*, *m*-Xylene
--	Cyclopentene	6.5	Styrene
2.0	Cyclopentane	4.0	*o*-Xylene
4.5	2,3-Dimethylbutane	--	*n*-Nonane
13.0	2-Methylpentane	3.0	*i*-Propylbenzene
--	*c*-4-Methyl-2-pentene	5.0	*n*-Propylbenzene
10.0	3-Methylpentane	3.0	*p*-Ethyltoluene
--	1-Hexene	22.0	*m*-Ethyltoluene
11.0	*n*-Hexane	3.0	*o*-Ethyltoluene
--	*t*-2-Hexene	17.0	1,3,5-Trimethylbenzene
--	*c*-2-Hexene	7.0	1,2,4-Trimethylbenzene
6.5	Methylcyclopentane		1,2,3-Trimethylbenzene
4.5	2,4-Dimethylpentane		Methylstyrene
9.5	Benzene		1,3-Diethylbenzene
2.0	Cyclohexane		1,4-Diethylbenzene

Total identified hydrocarbons	ppb C	%
Σ Olefin	46	9
Σ Aromatic	134	27
Σ Paraffin	301	60
Acetylene	16	3
	497	

	ppb C
Total unidentified hydrocarbons	87
Total NMHC by summing individual species	584

Source: Westberg and Lamb (1982)

TABLE 3-22. NONMETHANE HYDROCARBON CONCENTRATIONS MEASURED IN NONURBAN ATMOSPHERES

Location	Species analyzed	Concentration range, ppb C	Reference
Belfast, ME	$C_2 - C_5$	10 to 22	Sexton and Westberg (1984)
Benicia, CA	$C_2 - C_5$	7 to 14	Sexton and Westberg (1984)
Miami, FL	$C_2 - C_5$	2 to 23	Sexton and Westberg (1984)
Glascow, IL	$C_2 - C_{10}$	60 to 150	Chatfield and Rasmussen (1977)
Janesville, WI	$C_2 - C_{10}$	9 to 24	Sexton and Westberg (1984)
Houston, TX	$C_2 - C_{10}$	2 to 24	Sexton and Westberg (1984)
Robinson, IL	$C_2 - C_{10}$	13 to 113	Sexton and Westberg (1984)
Smoky Mtns.	$C_2 - C_{10}$	38 to 149	Cronn (1982)
Northern Idaho	Terpenes	0.1 to 18	Holdren et al. (1979)
Virginia	Isoprene	4 to 150	Ferman (1981)
Atlanta (urban)	Isoprene	0 to 8	Westberg and Lamb (1983)
Whiteface Mtn., NY	Terpenes	6 to 84	Whitby and Coffey (1977)
Elkton, MO	Isoprene	0 to 28	Rasmussen et al. (1976)
Southern WA	Isoprene		Allwine et al. (1983)
Eastern TX	α-pinene	0.1 to 8	Seila (1981)
North Carolina	α-pinene	0.6 to 13	Seila (1981)
Colorado	Terpenes	0 to 8	Roberts et al. (1983)

Because they are present at very low concentrations, it is extremely difficult to establish positive identifications when the natural hydrocarbons mix with manmade emissions in an urban area. The one exception is isoprene, which has been reported in both urban and nonurban sampling programs. Monoterpene ($C_{10}H_{16}$) concentrations in ambient air seldom exceed 20 ppb C. Average concentrations of α-pinene, the most commonly reported monoterpene, are usually below 10 ppb C. During the summer months, isoprene concentrations as high as 150 ppb C have been measured (Ferman, 1981). Maximum concentrations in the 30 to 40 ppb C range, however, are more common. Ambient concentrations of these naturally emitted hydrocarbons are very site-dependent. The highest concentrations are observed in or are immediately adjacent to forested areas. Seasonal variations will exist, as well, because natural hydrocarbon emission fluxes are directly related to the amount of biomass present and increase with temperature. In a recent review article, Altshuller (1983) has provided a more detailed discussion of natural hydrocarbons and their effect on air quality.

3.5.1.3 Nonmethane Hydrocarbon Concentrations Aloft. Hydrocarbon concentrations in the layer above a morning surface inversion and below the afternoon mixing level are of interest because oxidant precursors in this layer mix with urban plumes following breakup of the surface inversion. Table 3-23 provides a listing of mean hydrocarbon concentrations and the range of concentrations observed aloft in the vicinity of several United States cities. Data included in Table 3-23 were obtained from samples collected between 6:00 and 10:00 a.m. at altitudes between 1000 and 5000 ft above the surface. Mean NMHC values vary from about 10 ppb C to nearly 50 ppb C, with individual samples spanning the range of approximately 10 to 100 ppb C. These data were acquired during oxidant study programs and therefore represent hydrocarbon concentrations aloft during summertime periods when oxidant episodes are most likely to occur.

The hydrocarbon content of samples collected aloft is dominated by alkanes. Based on the 150 or so samples summarized in Table 3-23, alkanes were about 75 percent of the total NMHC, aromatics accounted for about 15 percent, and alkenes the remaining 10 percent.

3.5.1.4 Urban Aldehyde Concentrations. Aldehydes are produced in urban atmospheres by photochemical reactions. In addition to this in situ source, aldehydes are emitted by combustion sources and, thus, enter the atmosphere as primary pollutants. Most of the ambient aldehyde data are restricted to

TABLE 3-23. NONMETHANE HYDROCARBON CONCENTRATIONS IN SAMPLES COLLECTED ALOFT (1000 to 5000 ft) DURING MORNING HOURS (6:00 to 10:00 a.m.)

Location and date	Mean NMHC conc., ppb C	Range of NMHC concns., ppb C	No. samples
Atlanta (1981)	19	9 to 41	14
Baltimore (1980)	41	11 to 90	28
Boston (1980)	19	4 to 42	11
Canton, OH (1974)	34	24 to 48	15
Groton, CT (1975)	23	13 to 41	8
Houston (1978)	35	14 to 81	15
Milwaukee (1981)	22	10 to 66	9
New York (1980)	50	11 to 88	18
Philadelphia (1979)	32	21 to 59	6
Phoenix (1973)	32	12 to 47	7
Tulsa	44	13 to 73	10
Washington, D.C. (1980)	36	11 to 65	15

Source: Adapted from Westberg and Allwine (1984).

formaldehyde concentrations measured by the chromotropic acid (CA) method and total aliphatic aldehydes obtained by means of the 3-methyl-2-benzothiazolone (MBTH) monitoring procedure. Long-path infrared techniques have provided some ambient aldehyde data for the Los Angeles area. Analytical procedures that permit the routine characterization of individual aldehydes have only recently been reported. When ambient air is passed through a dinitrophenylhydrazine solution, aldehydes are converted to hydrazones that can be separated and quantitatively determined by liquid chromatography (HPLC). Ambient aldehyde data that have been acquired from all of these monitoring procedures will be utilized in the ensuing discussion.

Aldehydes observed in urban atmospheres include formaldehyde, acetaldehyde, acrolein, chloral, propanal, n-butanal, and benzaldehyde. Formaldehyde concentrations have been best characterized because the CA monitoring methodology was established in the early 1960s. Table 3-24 shows formaldehyde levels recorded in a number of United States cities. Most of the studies referenced in this table were of short duration. Consequently, the mean concentrations that are listed may not be representative of seasonal or annual means. Even from this limited data base, however, it is apparent that urban formaldehyde concentrations are low. With the exception of the 1961 Los Angeles data, the reported mean values fall in the 10 to 30 ppb range, with maximum concentrations ranging up to 90 ppb. Since mean nonmethane hydrocarbon (NMHC) levels in many of these same cities range between 400 and 900 ppb C, formaldehyde probably constitutes less than 3% of the total NMOC (NMHC plus aldehydes) in most urban areas. This supposition is supported by recent work in Los Angeles which showed a mean NMHC concentration of approximately 2900 ppb C and, during the same time period, a mean formaldehyde level of 27.5 ppb C. In this case, the formaldehyde amounted to less than 1 percent of the total NMOC.

Diurnal monitoring programs in Los Angeles and other cities indicate that formaldehyde concentrations are elevated during the morning rush-hour traffic period and again during the afternoon hours when ozone levels are high. Generally, the highest formaldehyde levels coincide closely with peak ozone concentrations. In the Los Angeles basin, formaldehyde concentrations in the 20 ppb range have been observed throughout the nighttime hours (Tuazon et al., 1981).

Acetaldehyde concentrations are generally below formaldehyde levels in a given urban area. Data collected in Las Vegas during 1980 and 1981 showed an

TABLE 3-24. FORMALDEHYDE CONCENTRATIONS IN SEVERAL UNITED STATES CITIES

City	Date	Mean concentration, ppb	Concentration range, ppb	Measurement method	Reference
Los Angeles	1961	40	5-160	CA	a
Los Angeles	1978	23	6-71	Long-path IR	b
Los Angeles	1981	28	4-86	HPLC	c
Columbus, OH	1980	8	1-24	CA	d
Baltimore	1980	27	1-87	CA	d
Denver	1980	12	7-29	CA/HPLC	e
St. Louis	1980	11	8-19	CA/HPLC	e
Chicago	1981	13	9-17	CA/HPLC	e
Riverside	1980	19	10-41	CA/HPLC	e
New York	1981	14	7-46	CA/HPLC	e
Pittsburgh	1981	21	13-35	CA/HPLC	e
Houston	1978	10	-----	CA	f
Las Vegas	1981	11	0-35	HPLC	g

[a] Altshuller and McPherson (1963).

[b] Tuazon et al. (1978).

[c] Grosjean and Fung (1984).

[d] Joshi et al. (1981).

[e] Singh et al. (1982).

[f] Joshi et al. (1979).

[g] Naylor et al. (1981).

average acetaldehyde concentration of 6 ppb, with a range from 0 to 14 ppb. This compares to an average formaldehyde concentration of 11 ppb during the same study period. During the fall months of 1981 in Los Angeles, acetaldehyde concentrations ranged between 2 and 39 ppb, while the formaldehyde levels varied between 4 and 86 ppb. On a ppb C basis, acetaldehyde comprised 23 percent of average carbonyl content and 0.6 percent of the total NMOC measured in the 1981 Los Angeles study (Grosjean and Fung, 1984).

Ambient air concentrations of higher-molecular-weight aldehydes were reported in both the Los Angeles and Las Vegas studies referred to previously. In Los Angeles, C_3 carbonyls (propanal, acetone, and acrolein) varied in concentration from 1 to 54 ppb, butanal ranged between 0 and 5 ppb, and benzaldehyde concentrations never exceeded 2 ppb. Propanal concentrations up to about 1 ppb and benzaldehyde levels ranging between 0 and 0.6 ppb were measured in Las Vegas. Chloral (trichloroacetaldehyde) was detected in ambient air in Las Vegas at an average concentration of 1 ppb, with values for 18 samples ranging between 0 and 5 ppb. Acrolein, which is believed to cause eye irritation, has been measured in Los Angeles air at concentrations up to 15 ppb.

Since the early 1960s, the MBTH method has been employed in urban environments to measure total aliphatic aldehyde concentrations. The total aldehyde concentrations determined in this way include formaldehyde, which is generally the predominant aldehyde present. In studies where simultaneous formaldehyde (CA method) and total aliphatic aldehyde (MBTH method) data are available, formaldehyde usually accounts for more than 50 percent of the total aldehydes. Measurements in Columbus, Ohio, during the summer of 1980 showed a mean formaldehyde level of 7.9 ppb and a mean total aldehyde concentration of 13 ppb. In Houston, Joshi (1979) found an average of 10 ppb formaldehyde and 16.4 total aldehydes. These were short-term studies (1 to 2 months) conducted during the oxidant season. On an annual basis, the formaldehyde contribution is even more significant. For example, the annual mean total aldehyde concentration (MBTH 24-hour method) averaged across all Houston monitoring stations in 1974 was identical to the mean formaldehyde concentration.

In summary, it appears that urban aldehyde concentrations can vary from a few ppb up to about 200 ppb. Formaldehyde is present in highest concentration, followed by acetaldehyde. In polluted atmospheres, acrolein, propanal, butanal, and benzaldehyde have been measured at concentrations less than 15 ppb. Where concurrent nonmethane hydrocarbon (NMHC) data are available, aldehydes average about 3 percent of the total nonmethane organic (NMOC) species present.

3.5.1.5 Aldehyde Concentrations in Rural Atmospheres.

Formaldehyde levels in remote atmospheres have been reported to range between 0.1 and 10 ppb. Mean concentrations representative of global background conditions vary from 0.3 to 0.5 ppb (Duce et al., 1983). Very few total aldehyde measurements have been made at rural locations in the United States. Breeding et al. (1973) reported values of 1 to 2 ppb in rural Illinois and Missouri. It is expected that certain higher-molecular-weight aldehydes (C_6-C_{10}) emitted by natural vegetation should be present in the gas phase; however, ambient concentrations of these species have not been reported.

3.5.2 Atmospheric Concentrations of Nitrogen Oxides

Ambient air levels of nitrogen oxides have been monitored throughout the United States for a number of years. Since NO_2 is the only oxide of nitrogen for which a NAAQS has been promulgated, it has received the greatest attention. The National Aerometric Data Bank at EPA, which receives ambient air data from federal, state and local monitoring stations, contains the most comprehensive collection of aerometric data for the United States. The air quality criteria document for oxides of nitrogen (U.S. Environmental Protection Agency, 1982) included a thorough discussion of seasonal and annual trends in ambient NO_x concentrations for a large number of United States cities. This type of information will not be repeated in this present discussion. The emphasis here will be on NO_x measurements that can be related to the diurnal photochemical processes that produce ozone.

3.5.2.1 Urban NO_x Concentrations.

Concentrations of NO_x, like hydrocarbon concentrations, tend to peak in urban areas during the early morning period when atmospheric dispersion is limited and automobile traffic is dense. Most of the NO_x is emitted as nitric oxide (NO) and, thus, in the absence of chemical reactions NO would be expected to be the predominant oxide of nitrogen present. Nitric oxide is converted rapidly, however, to NO_2 by ozone and peroxy radicals produced in atmospheric photochemical reactions. Since both the abundance of ozone and the photochemical activity vary diurnally and from day to day, the relative concentrations of NO and NO_2 can fluctuate significantly. As a general rule, urban NO concentrations peak during the 6:00 to 9:00 a.m. period in the morning. This is followed by a rapid decrease caused by the photochemical conversion of NO and NO_2 and increased atmosphere mixing. Nitric oxide levels remain low during the daytime period and then usually begin to build up again through the nighttime hours. Nitrogen dioxide concentrations typically increase during the mid-morning hours and then abate as the afternoon progresses. Levels of NO_2 begin to increase again following the late afternoon rush-hour period and often continue to climb during the nighttime.

The average NO_x concentration in urban areas of the United States is about 70 ppb, with nitric oxide and nitrogen dioxide contributing about equally (Logan, 1983). Monitoring data for 1975 through 1980 showed that peak 1-hr NO_2 concentrations equalled or exceeded 400 ppb in Los Angeles and several other California locations, as well as at sites in Kentucky (Ashland) and Michigan (Port Huron). Cities with one peak hourly concentration exceeding 270 ppb during those years include Phoenix, St. Louis, New York City, Springfield, IL, Cincinnati, Saginaw, and Southfield, MI, and more than a dozen sites in California. Reported hourly concentrations in excess of 140 ppb were quite common nationwide during the years between 1975 and 1980 (U.S. Environmental Protection Agency, 1982).

Urban NO_x concentrations during the 6:00 to 9:00 a.m. period are of primary importance in terms of oxidant production. Average NO_x levels recorded in several urban areas during this morning period are listed in Table 3-25. Most of these data were collected in special, field study programs that were designed to provide information concerning ozone and ozone-precursor relationships. Thus, concurrent 6:00 to 9:00 a.m. hydrocarbon samples were also obtained, which permits the calculation of hydrocarbon-NO_x ratios in each of these urban areas. These data are included in Table 3-25.

As can be seen in Table 3-25, mean 6:00 to 9:00 a.m. NO_x concentrations in the 10 cities listed fall in the range of about 50 to 150 ppb. Hydrocarbon concentrations (ppb C) exceeded the oxides of nitrogen levels by a factor of 5 to 16 during this same time period. Smog chamber experiments indicate that significant quantities of ozone can be produced when HC/NO_x ratios are in this range. Threfore, when meteorological conditions are appropriate, it is expected that an ozone buildup will occur in plumes emanating from these cities. Indeed, ozone production has been observed in the vicinity of most of the cities referenced in Table 3-25.

3.5.2.2 Nonurban NO_x Concentrations. Concentrations of NO_x in "clean" remote environments are usually below 0.5 ppb (Logan, 1983). For example, median concentrations measured on Niwot Ridge in Colorado are about 0.3 ppb in the

TABLE 3-25. AVERAGE 6:00 to 9:00 a.m. NO_x CONCENTRATIONS AND HC/NO_x RATIOS IN URBAN AREAS

City	Average NO_x, ppb	Average HC/NO_x	References
Atlanta	57	9	Westberg and Lamb (1983)
Baltimore	85	10	Richter (1983)
Boston	63	10	Richter (1983)
Houston	125	13	Westberg et al. (1978)
Linden, NJ	59	16	Richter (1983)
Los Angeles	147	10	U.S. Environmental Protection Agency (1978)
Milwaukee	66	5	Westberg and Lamb (1983)
St. Louis	77	8	EPA (1978)
Tulsa	46	13	Eaton et al. (1979)
Washington, D.C.	94	14	Richter (1983)

summer and 0.24 ppb in winter. In exceptionally clean air, NO_x concentrations as low as 0.015 have been recorded (Bollinger et al., 1982). Slightly higher NO_x concentrations have been reported at other remote locations in the western United States and Canada. Kelly et al. (1982) deduced a mean NO_x concentration of about 1 ppb from measurements in South Dakota. At the South Dakota site, nitric oxide generally contributed less than 20 percent of the total NO_x. Measurements of NO_x during the 1970s at rural locations in Montana (Decker et al., 1978) and Saskatchewan (McElroy and Kerr, 1977) yielded average concentrations similar to those recorded in South Dakota.

In the northeastern United States, nonurban NO_x concentrations appear to exceed those in the west by about a factor of ten. A median NO_x concentration of 6.6 ppb was derived from data collected at nine rural sites utilized in the Sulfate Regional Experiment (SURE) program (Mueller and Hidy, 1983). Median concentrations at the individual stations, which extended eastward from the Ohio River Valley to the Atlantic Coast, varied from 2 to 11 ppb. Measurements at nonurban sites in Pennsylvania and Louisiana during the summer of 1975 showed mean hourly NO_x concentrations of 4.7 and 4.1 ppb, respectively (Decker et al., 1978). Nitric oxide composed approximately 40 percent of the total NO_x at these latter two nonurban sites.

In summary, it appears from the limited amount of data available that NO_x concentrations in unpopulated, rural regions of the western United States average 1 ppb or less. At nonurban locations in the more industralized eastern United States, average NO_x concentrations can exceed 10 ppb.

3.6 SUMMARY

3.6.1 Nature of Precursors to Ozone and Other Photochemical Oxidants

Photochemical oxidants are products of atmospheric reactions involving volatile organic compounds (VOC), oxides of nitrogen (NO_x), hydroxyl radicals, oxygen, and sunlight. They are almost exclusively secondary pollutants, formed in the atmosphere from their precursors by processes that are a complex function of precursor emissions and meteorological factors.

Although vapor-phase hydrocarbons (compounds of carbon and hydrogen only) are the predominant organic compounds in the ambient air that serve as precursors to photochemical oxidants, other volatile organic compounds are also photochemically reactive in those atmospheric processes that give rise to the oxidants. In particular, halogenated organics (e.g., haloalkenes) that participate in photochemical reactions are present in ambient air, although at lower concentrations than the hydrocarbons. They are apparently oxidized through the same initial step involved in the oxidation of the hydrocarbons; that is, attack by hydroxyl radicals (HO·). Alkenes, haloalkenes, and aliphatic aldehydes are, as classes, among the most reactive organic compounds found in ambient air. Alkenic hydrocarbons and halocarbons are unique among VOC in ambient air in that they are susceptible both to attack by HO· and to ozonolysis (oxidation by ozone) (Niki et al., 1983). Methane, halomethanes, and certain haloethenes are of negligible reactivity in ambient air and have been classed as unreactive by the U.S. Environmental Protection Agency (1980).

The oxides of nitrogen that are important as precursors to ozone and other photochemical oxidants are nitrogen dioxide (NO_2) and nitric oxide (NO). Nitrogen dioxide is itself an oxidant that produces deleterious effects, which are the subject of a separate criteria document (U.S. Environmental Protection Agency, 1982). Nitrogen dioxide is an important precursor to ozone and other photochemical oxidants (1) because its photolysis in ambient air leads to the formation of oxygen atoms that combine with molecular oxygen to form ozone; and (2) because it reacts with acetylperoxy radicals to form peroxyacetyl nitrate (PAN), a relatively potent phytotoxicant and lachrymator. Although ubiquitous, nitrous oxide (N_2O) is unimportant in the production of oxidants in ambient air because it is virtually inert in the troposphere. (In the stratosphere, where the wavelength distribution is different, N_2O is photolyzed.)

Since methane is considered only negligibly reactive in ambient air, the volatile organic compounds of importance as oxidant precursors are usually referred to as nonmethane hydrocarbons (NMHC) or, more properly, as nonmethane organic compounds (NMOC).

3.6.2 Measurement of Precursors to Ozone and Other Photochemical Oxidants

Numerous analytical methods have been employed to determine nonmethane organic compounds (NMOC) in ambient air. To present an overview of the most pertinent information, measurement methods for the organic species may be arranged in three major classifications: nonmethane hydrocarbons, aldehydes, and other oxygenated compounds.

Nonmethane hydrocarbons have been determined primarily by methods that employ a flame ionization detector (FID) as the sensing element. Early methods for the measurement of total nonmethane hydrocarbons did not provide for speciation of the complex mixture of organics in ambient air. These methods, still in use for anaysis of total nonmethane organic compounds, are essentially organic carbon analyzers, since the response of the FID detector is essentially proportional to the number of carbon atoms present in the organic molecule (Sevcik, 1975). Carbon atoms bound, however, to oxygen, nitrogen, or halogens give reduced relative responses (Dietz, 1967). This detector has been utilized both as a stand-alone continuous detection system (non-speciation) and also with gas chromatographic techniques that provide for speciation of the many organics present in ambient air. A number of studies of non-speciation analyzers have indicated an overall poor performance of the commercial instruments when calibration or ambient mixtures containing NMOC concentrations less than 1 ppm C were analyzed (e.g., Reckner, 1974; McElroy and Thompson, 1975; Sexton et al., 1981). The major problems associated with the non-speciation analyzers have been summarized in a recent technical assistance document published by the U.S. Environmental Protection Agency (1981). The document also presents ways to reduce some of the existing problems.

Because of the above deficiencies, other approaches to the measurement of nonmethane hydrocarbons are currently under development. The use of gas chromatography coupled to an FID system circumvents many of the problems associated with continuous non-speciation analyzers. This method, however, requires sample preconcentration because the organic components are present at part-per-billion (ppb) levels or lower in ambient air. The two main preconcentration techniques in present use are cryogenic collection and the use of solid adsorbents (McBride and McClenny, 1980; Jayanty et al., 1982; Westberg et al., 1980; Ogle et al., 1982). The preferred preconcentration method for obtaining speciated data is cryogenic collection. Speciation methods involving cryogenic preconcentration have also been compared with continuous non-speciation analyzers (e.g., Richter, 1983). Results indicate poor correlation between methods at ambient concentrations below 1 part-per-million carbon (ppm C).

Aldehydes, which are both primary and secondary pollutants in ambient air, are detected by total NMOC and NMHC speciation methods but can not be quantitatively determined by those methods. Primary measurement techniques for aldehydes include the chromotropic acid (CA) method for formaldehyde (Atlshuller and McPherson, 1963; Johnson et al., 1981), the 3-methyl-2-benzothiazolone (MBTH) technique for total aldehydes (e.g., Sawicki et al., 1961; Hauser and Cummins, 1964), Fourier-transform infrared (FTIR) spectroscopy (e.g., Hanst et al., 1982; Tuazon et al., 1978, 1980, 1981), and high-performance liquid chromatography employing 2,4-dinitrophenyl-hydrazine derivatization (HPLC-DNPH) for aldehyde speciation (e.g., Lipari and Swarin, 1982; Kuntz et al., 1980). The CA and MBTH methods utilize wet chemical procedures and spectrophotometric detection. Interferences from other compounds have been reported for both techniques. The FTIR method offers good specificity and direct in situ analysis of ambient air. These advantages are offset, however, by the relatively high cost and lack of portability of the instrumentation. On the other hand, the HPLC-DNPH method not only offers good specificity but can also be easily transported to field sites. A few intercomparison studies of the above methods have been conducted and considerable differences in measured concentrations were found. The data base is still quite limited at present, however, and further intercomparisons are needed.

Literature reports describing the vapor-phase organic composition of ambient air indicate that the major fraction of material consists of unsubstituted hydrocarbons and aldehydes. With the exception of formic acid, other oxygenated species are seldom reported. The lack of oxygenated hydrocarbon data is somewhat surprising since significant quantities of these species are emitted into the atmosphere by solvent-related industries and since at least some oxygenated species appear to be emitted by vegetation. In addition to direct emissions, it is also expected that photochemical reactions of hydrocarbons with oxides of nitrogen, ozone, and hydroxyl radicals will produce significant quantities of oxygenated products. The adsorptive nature of the surfaces that contact these oxygenated species during sample collection and analysis may account for the apparent lack of data. Attempts have been made to decrease adsorption by deactivating the reactive surface or by modifying the compound of interest (Osman et al., 1979; Westbert et al., 1980). Additional research efforts should focus on this area.

Aside from the essentially unreactive N_2O, only two oxides of nitrogen occur in ambient air at appreciable concentrations: nitric oxide (NO) and nitrogen dioxide (NO_2). Both compounds, together designated as NO_x, participate in the cyclic reactions in the atmosphere that lead to the formation of ozone.

The preferred means of measuring NO and NO_2 is the chemiluminescence method (U.S. Environmental Protection Agency, 1976). The measurement principle is the gas-phase chemiluminescent reaction of O_3 and NO (Fontijn et al., 1970). While NO is determined directly in this fashion, NO_2 is detected indirectly by first reducing or thermally decomposing the gas quantitatively to NO with a converter. The reaction of NO and O_3 forms excited NO_2 molecules that release light energy that is proportional to the NO concentration. Although the NO chemiluminescence is interference-free, other nitrogen compounds do interfere when directed through the NO_2 converter. The magnitude of these interferences is dependent upon the type of converter used (Winer et al., 1974; Joshi and Bufalini, 1976). Other NO and NO_2 measuring methods have also been summarized in this chapter. None of the other techniques is widely used to monitor air quality.

3.6.3 Sources and Emissions of Precursors

The photochemical production of ozone, the principal component of "smog," depends both on the presence of precursors, volatile organic compounds (VOCs) and nitrogen oxides (NO_x), that are emitted by manmade and by natural sources, and on suitable conditions of sunlight, temperature, and other meteorological factors. Because of the intervening requirement for meteorological conditions conducive to the photochemical generation of ozone, emission inventories are not as direct predictors of ambient concentrations in the case of secondary pollutants such as ozone and other oxidants as they are for primary pollutants.

Emissions of manmade VOCs (excluding several relatively unreactive compounds such as methane) in the United States have been estimated at 18.2 tg/yr for 1982. Trends in manmade VOC emissions for 1970 through 1982 were shown in Figure 3-3 (U.S. Environmental Protection Agency, 1983). The annual emission rate for manmade VOCs has decreased some 28 percent during this period. The main sources nationwide are industrial processes, which emit a wide variety of VOCs such as chemical solvents; and transportation; which includes the emission of VOCs in gasoline vapor as well as in gasoline combustion products. Estimates of biogenic emissions of organic compounds in the United States are highly inferential but data suggest that the yearly rate is the same order of magnitude as manmade emissions. Most of the biogenic emissions actually occur during the growing season, however, and the kinds of compounds emitted are different.

Emissions of manmade NO_x in the United States estimated at 20.2 tg/yr for 1982. Annual emissions of manmade NO_x were some 12 percent higher in 1982 than in 1970, but the rate leveled off in the late 1970s and exhibited a small decline from about 1980 through 1982. The increase over the period 1970 through 1982 had two main causes: (1) increased fuel combustion in stationary sources such as power plants; and (2) increased fuel combustion in highway motor vehicles, as the result of the increase in vehicle miles driven. Total vehicle miles driven increased by 42 percent over the 13 years in question. Trends in manmade NO_x emissions over 1970 through 1982 were shown in Figure 3-5 (U.S. Environmental Protection Agency, 1983). Estimated biogenic NO_x emissions are based on uncertain extrapolations from very limited studies, but appear to be about an order of magnitude less than manmade emissions.

3.6.4 Ambient Air Concentrations of Precursors

3.6.4.1 Hydrocarbons in Urban Areas. Most of the available ambient air data on the concentrations of nonmethane hydrocarbons (NMHC) in urban areas have been obtained during the 6:00 to 9:00 a.m. period. Since hydrocarbon emissions are at their peak during that period of the day, and since atmospheric dispersion is limited that early in the morning, NMHC concentrations measured then generally reflect maximum diurnal levels. Representative data for urban areas show mean NMHC concentrations between 0.4 and 0.9 ppm.

The hydrocarbon composition of urban atmospheres is dominated by species in the C_2 to C_{10} molecular-weight range. The paraffinic hydrocarbons (alkanes) are most prominent, followed by aromatics and alkenes. Based on speciation data obtained in a number of urban areas, alkanes generally constitute 50 to 60 percent of the hydrocarbon burden in ambient air, aromatics 20 to 30 percent, with alkenes and acetylene making up the remaining 5 to 15 percent (Sexton and Westberg, 1984).

3.6.4.2 Hydrocarbons in Nonurban Areas. Rural nonmethane hydrocarbon concentrations are usually one to two order of magnitude lower than those measured in urban areas (Ferman, 1981; Sexton and Westberg, 1984). In samples from sites carefully selected to guarantee their rural character, total NMHC concentrations ranged from 0.006 to 0.150 ppm C (e.g., Cronn, 1982; Seila, 1981; Holdren et al., 1979). Concentrations of individual species seldom exceeded 0.010 ppm

C. The bulk of species present in rural areas are alkanes; ethane, propane, n-butane, iso-pentane, and n-pentane are most abundant. Ethylene and propene are sometimes present at ≤0.001 ppm C, and toluene is usually present at ~0.001 ppm C. Monoterpene concentrations are usually about ≤0.020 ppm C. During the summer months, isoprene concentrations as high as 0.150 ppm C have been measured (Ferman, 1981). The maximum concentrations of isoprene usually encountered, however, are in the range of 0.030 to 0.040 ppm C.

3.6.4.3 Aldehydes in Urban Areas. Aldehydes observed in urban atmospheres include formaldehydes, acetaldehyde, chloral, propanal, n-butanal, and benzaldehyde. Formaldehyde concentrations are the best characterized of these aldehydes because the chromotropic acid methodology for formaldehyde was established in the early 1960s. With the exception of early data from Los Angeles (1961), reported concentrations of formaldehyde in urban areas fall in the 0.01 to 0.03 ppm range, with maximum concentrations ranging up to 0.09 ppm.

Comparing these concentrations with concentrations of NMHC in urban areas, it is apparent that formaldehyde probably constitutes less than 3 percent of the total NMOC in most urban areas. Acetaldehyde concentrations are generally lower than formaldehyde in a given urban area. Concentrations of total aldehydes in urban atmospheres can vary from a few ppb up to about 0.2 ppm (200 ppb). In polluted atmospheres, acrolein, propanal, butanal, and benzaldehyde have each been measured at concentrations <0.015 ppm.

3.6.4.4 Aldehydes in Nonurban Areas. Very few total aldehyde measurements have been made in rural areas. Breeding et al. (1973) reported values for total aldehydes of 0.001 to 0.002 ppm in rural Illinois and Missouri. Formaldehyde levels in remote atmospheres apparently range from 0.1 to 10 ppb, with global background formaldehyde concentrations varying from 0.3 to 0.5 ppb (Duce et al., 1983).

3.6.4.5 Nitrogen Oxides in Urban Areas. Concentrations of NO_x, like hydrocarbon concentrations, tend to peak in urban areas during the early morning, when atmospheric dispersion is limited and automobile traffic is dense. Most NO_x is emitted as nitric oxide (NO), but the NO is rapidly converted to NO_2 by ozone and peroxy radicals produced in atmospheric photochemical reactions. The relative concentrations of NO versus NO_2 fluctuate day-to-day, depending on diurnal and day-to-day fluctuations in ozone levels and photochemical activity.

Urban NO_x concentrations during the 6:00 to 9:00 a.m. period in 10 cities ranged from 0.05 to 0.15 ppm in studies done in the last 5 to 7 years (e.g., Westberg and Lamb, 1983; Richter, 1983; Eaton et al., 1979). Concurrent NMHC measurements for these 10 cities showed that $NMHC/NO_x$ ratios ranged from 5 to 16.

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4. CHEMICAL AND PHYSICAL PROCESSES IN THE FORMATION AND OCCURRENCE OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

4.1 INTRODUCTION

In the preceding chapter, the nature and identity of precursors to ozone and other photochemical oxidants were discussed, sources of those precursors were identified, the amount of precursors emitted into the atmosphere from various sources was estimated, and the concentrations of precursors actually measured in the ambient air were described.

The present chapter provides an overview of the complex chemical and physical processes by which ozone and other photochemical oxidants are formed from their precursors. In addition, the present chapter describes the physical processes that result in the transport and dispersion of ozone and the other oxidants once they are formed. That discussion also includes a brief summary of the processes by which stratospherically formed ozone can be brought into the troposphere, through the boundary and sub-laminar layers, and to the surface.

The subsequent chapter (Chapter 5) presents summary information on the reactions of ozone and other photochemical oxidants in ambient air and in biological systems. The present chapter includes, however, a brief discussion of the relationship of ozone and the other oxidants to atmospheric phenomena that result from the formation of secondary organic and inorganic aerosols, a process to which ozone and other oxidants contribute indirectly.

4.2 CHEMICAL PROCESSES

> The photochemistry of the polluted atmosphere is exceedingly complex. Even if one considers only a single hydrocarbon pollutant, with typical concentrations of nitrogen oxides, carbon monoxide, water vapor, and other trace components of air, several hundred chemical reactions are involved in a realistic assessment of the chemical evolution of such a system. The actual urban atmosphere contains not just one but hundreds of different hydrocarbons, each with its own reactivity and oxidation products.
>
> (National Academy of Sciences, 1977)

In order to understand the effects of ozone and other photochemical oxidants on humans, vegetation, and other receptors, however, it is not necessary to comprehend all the complex chemical reactions that take place during formation of these species in the atmosphere. It is sufficient to understand how photochemical oxidants result from the action of sunlight on precursor compounds. For a complete and detailed discussion of the many complex reactions thought to take place in polluted atmospheres, the reader is referred to Demerjian et al. (1974) and to Atkinson and Lloyd (1984). For a simple explanation of the origin of these secondary pollutants, the following summarizes current understanding of the photochemical processes leading to their production.

4.2.1 Formation of Ozone and Oxidants

The concentrations of ozone and oxidants found in urban areas and in downwind and rural receptor regions are the net result of at least three general processes: first, the initial emission, dispersion, and then transport of precursors of ozone and oxidants; second, the photochemical reaction processes that occur in the atmosphere as the dispersion and transport take place; and third, the scavenging processes along the trajectory that act to reduce the concentrations of both precursors and the resulting ozone and oxidants. This section discusses briefly the chemical reactions that take place, while the following section (4.3) discusses the meteorological and climatological processes that influence the formation and distribution of ozone and other photochemical oxidants.

In the troposphere, ozone is formed indirectly through the action of sunlight on nitrogen dioxide (NO_2). Sunlight decomposes NO_2 into nitric oxide (NO) and an oxygen atom:

$$NO_2 + \text{sunlight} \longrightarrow NO + O \qquad (4\text{-}1)$$

The oxygen atom (O) liberated in this process combines with an oxygen molecule to produce ozone:

$$O + O_2 + M \longrightarrow O_3 + M \qquad (4\text{-}2)$$

In the absence of any competing reactions, the ozone formed in reaction (4-2) combines with the NO liberated in reaction (4-1) to regenerate an NO_2 molecule:

$$O_3 + NO \longrightarrow NO_2 + O_2 \qquad (4\text{-}3)$$

As a result of the above three reactions, an equilibrium or steady-state condition is established among NO, NO_2, and O_3, and the concentration of O_3 in the atmosphere is governed by the expression,

$$[O_3] = K \frac{[NO_2]}{[NO]}, \qquad (4\text{-}4)$$

where K is a constant that depends on the sunlight intensity. Typically, K in the lower troposphere is less than or equal to 0.025 ppm. It is apparent from equation (4-4) that very little buildup of ozone can occur until most of the NO that has been emitted into the atmosphere is converted to NO_2. Equations (4-1) through (4-3), however, cannot by themselves explain the buildup of ozone, since for each molecule of NO oxidized to NO_2 in equation (4-3) a molecule of ozone is also destroyed.

An alternate pathway of conversion of NO to NO_2 that does not destroy O_3 is needed to explain the high ozone levels observed in the urban environment. Such an alternate pathway is available through the oxidation of reactive organic species such as hydrocarbons. In the atmosphere, these species can be oxidized by hydroxyl radicals (HO·). There are a number of sources of HO radicals in the lower troposphere. One such source is nitrous acid. This species, which is formed in the tailpipes of automobiles, reacts with sunlight in the atmosphere to produce HO radicals. The HO radicals formed in this and other processes react with hydrocarbons to generate an alkyl radical (R·):

$$HO\cdot + \text{hydrocarbon} \longrightarrow R\cdot + H_2O \qquad (4\text{-}5)$$

This hydrocarbon radical, R·, quickly picks up an oxygen molecule to form a peroxy radical, $RO_2\cdot$:

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (4\text{-}6)$$

The next reaction in the series is generally thought to be a conversion of NO to NO_2, at the same time producing an alkoxy radical:

$$RO_2\cdot + NO \longrightarrow RO\cdot + NO_2 \qquad (4\text{-}7)$$

The alkoxy radical reacts with an oxygen molecule to produce a hydroperoxy radical and an aldehyde:

$$RO\cdot + O_2 \longrightarrow R'CHO + HO_2\cdot \qquad (4\text{-}8)$$

Finally, the cycle is completed when the hydroperoxy radical oxidizes another molecule of NO to NO_2 and forms a hydroxy radical, which then begins the cycle over again:

$$HO_2\cdot + NO \longrightarrow HO\cdot + NO_2 \qquad (4\text{-}9)$$

Other, more complex reactions may also occur (see Atkinson and Lloyd, 1984).

This description is highly simplified, but the reactions listed above contain the main features of the NO-to-NO_2 oxidation by organic and other radicals that leads to subsequent ozone formation. The essential ingredients are sunlight, NO or NO_2, and organic compounds. The latter two are emitted in abundance in urban areas as shown in section 3.4. The number and kind of hydrocarbon species formed during the course of atmospheric photochemical reactions is quite large. Present analytical techniques permit identification and measurement of individual hydrocarbon species at part-per-billion concentrations. In a recently published compendium, Graedel (1978) has documented the emission into or detection in ambient air of more than 1000 organic compounds.

4.2.2 Initiation and Termination of Photochemical Reactions

The initial source of radicals is an important aspect of the photochemistry of polluted atmospheres. Although the rate and yield of oxidant formation depend on many factors, the length of the induction period before the accumulation of oxidant begins depends heavily on the initial concentration of radicals. In smog chambers, the photolysis of nitrous acid, HONO, may be the most important initial source of radicals (Pitts et al., 1977). There is also evidence to suggest that HONO may be a source of free radicals in the atmosphere as well (Perner and Platt, 1979; Harris et al., 1982). Nitrous acid has been observed in urban atmospheres at concentrations up to 8 ppb (Platt et al., 1980; Harris et al., 1982).

Probably the most important source of radicals in the atmosphere is the photolysis of aldehydes:

$$RCHO + \text{sunlight} \longrightarrow HCO\cdot + R\cdot \qquad (4\text{-}10)$$

The HCO radicals liberated in this process rapidly react with oxygen:

$$HCO\cdot + O_2 \longrightarrow HO_2\cdot + CO \qquad (4\text{-}11)$$

As explained in the previous section (4.2.1), the subsequent reaction of $HO_2\cdot$ (and $RO_2\cdot$ as well) with NO is the major route to the oxidation of nitric oxide in ambient air. Aldehydes are emitted from many sources, including automobiles (section 3.4.1). They are also formed as secondary pollutants in smog.

During the course of the overall smog formation process, the supply of free radicals is maintained by several sources, but the dominant one appears to be the photolysis of aldehydes formed in the atmosphere from the initial hydrocarbons. Since the reactions of free radicals with NO form a cyclic process, any additional source of radicals will add to the supply of radicals and will increase the rate of the cycle. Conversely, any reaction that removes free radicals will slow the rate of the cycle.

Although these photochemical reactions require sunlight, the presence of sunlight does not mean that the reactions continue indefinitely. Terminating reactions gradually remove NO and NO_2 from the reaction mixtures such that the cycles would slowly come to an end unless fresh NO_x emissions were injected into the atmosphere.

Termination of the chain reactions frequently leads to the formation of other oxidants as well as relatively stable organic nitrates in the atmosphere. Nitrous acid (HONO), nitric acid (HNO_3), peroxynitric acid ($HOONO_2$), hydrogen peroxide (H_2O_2), peroxyacetyl nitrate, ($CH_3COO_2NO_2$), other peroxyacyl nitrates, organic hydroperoxides, and organic peracids have all been observed either in smoggy atmospheres or in irradiated laboratory mixtures (National Academy of Sciences, 1977). These compounds are almost always found in very low concentrations in ambient air and may actually occur only as intermediates in the photochemical degradation of organic compounds. Even though they occur at low concentrations, however, many of these play significant or even critical roles in atmospheric chemistry (Pitts et al., 1983).

Figure 4-1 (Niki et al., 1978) shows some of the reactions involved in the HO·-initiated photooxidation of cis- or trans-2-butene in an atmosphere containing NO and NO_2. It can be seen that this involves a chain process and that the major organic product is acetaldehyde. As indicated by Niki et al. (1978) and Carter et al. (1979), the pathway leading to formic acid does not occur to any observable extent.

4.2.3 Limitations to Ozone Accumulation

The nature of photochemical systems can be partially explained by considering their behavior as a function of the initial concentrations of NO_x and hydrocarbons, as well as the ratio of these two reactants, i.e., the NMOC/NO_x ratio. At low NMOC/NO_x ratios (usually ratios of less than about 1:1 to 2:1), the rate at which NO is converted to NO_2 is influenced by the availability of organic compounds. In such a hydrocarbon-deficient and NO_x-rich system, few organic free radicals are available to effect the conversion of NO to NO_2. The oxidation of NO proceeds at such a slow rate that a high NO_2/NO ratio may not be achieved by sunset and the buildup of ozone may therefore be limited. At moderately high NMOC/NO_x ratios (usually greater than about 5:1 to 8:1), sufficient organic radicals are available to oxidize all of the NO. The NO_2/NO ratio, therefore, is favorable to O_3 accumulation.

At very high NMOC/NO_x ratios, NO will be oxidized rapidly to NO_2. The large number of organic radicals present in this system, however, will then quickly consume a substantial portion of the NO_2. Nitrate formation will increase, which will effectively lower the NO_2/NO ratio and limit O_3 buildup. Ozone formation also will be limited as a result of the reaction of O_3 with excess olefins.

4.2.4 Recent Work on Photochemical Smog Reactions

The hydrocarbons so important in the chemistry of the polluted troposphere are alkanes (paraffins), alkenes (olefins), and aromatics (section 3.2). In addition, the oxygenated hydrocarbons such as aldehydes, ketones, dicarbonyls, and perhaps some alcohols are also important, although they are always found in much smaller concentrations in ambient air than the hydrocarbons (section 3.5).

The photooxidation reactions of the alkanes is fairly well understood (Hampson and Garvin, 1978; Atkinson et al., 1982). The only significant

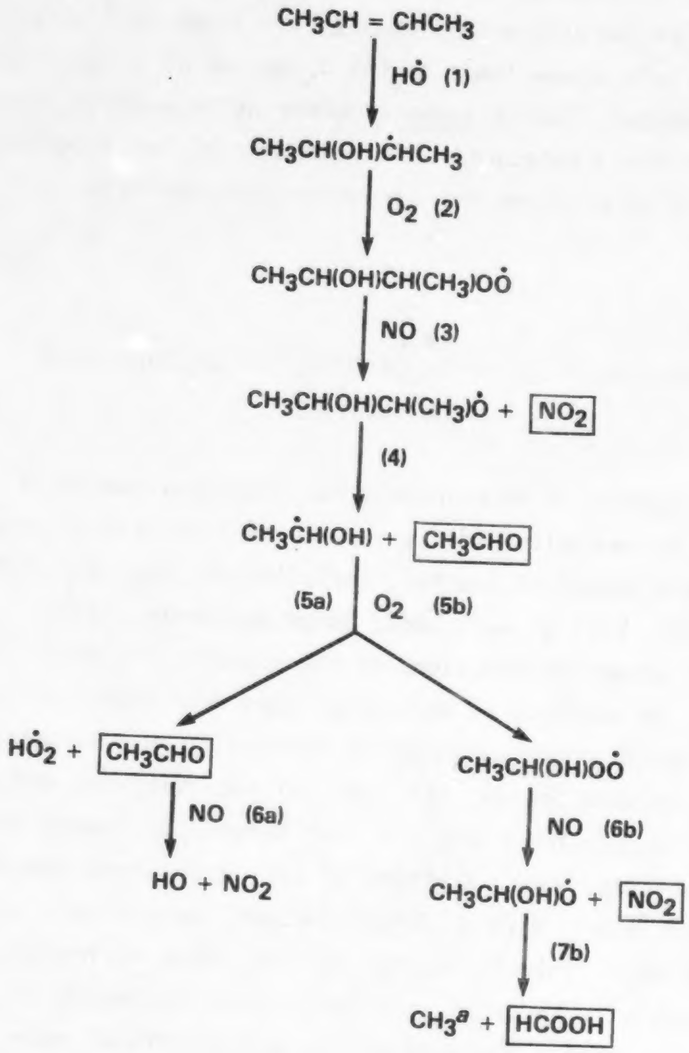
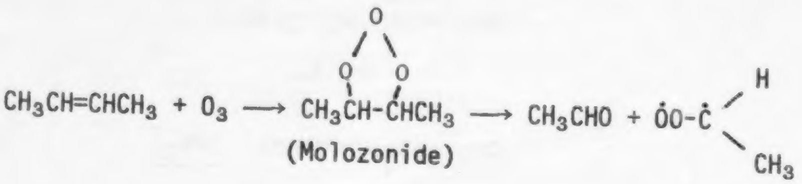

CH3CH = CHCH3
HȮ (1)
CH3CH(OH)ĊHCH3
O2 (2)
CH3CH(OH)CH(CH3)OȮ
NO (3)
CH3CH(OH)CH(CH3)Ȯ + NO2
(4)
CH3ĊH(OH) + CH3CHO
(5a) O2 (5b)
HȮ2 + CH3CHO
NO (6a)
HO + NO2
CH3CH(OH)OȮ
NO (6b)
CH3CH(OH)Ȯ + NO2
(7b)
CH3a + HCOOH

Figure 4-1. Reaction scheme for the HO·-initiated oxidation of 2-butene-NO system. ([a]The overall stoichiometry for CH_3 oxidation is $CH_3 + 2O_2 + 2NO \rightarrow CH_2O + HO + 2NO_2$; Niki et al., 1972; Demerjian et al., 1974.)

Source: Niki et al. (1978).

reaction involving alkanes is oxidation by HO radicals. These radicals abstract a hydrogen atom from the alkane to produce an alkyl radical and H_2O as shown in reaction 4-5. Alkenes, the most reactive class of hydrocarbons in the lower troposphere, undergo reaction with both HO· and O_3. The reaction pathways important in the alkene-OH· reaction are shown in Figure 4-1. The reaction of alkenes with ozone leads to the formation of a number of free radicals and stable products. Taking trans-2-butene as an example, ozone adds to the double bond to form a molozonide. The molozonide then undergoes rapid decomposition to form an aldehyde and a biradical intermediate:



$$CH_3CH{=}CHCH_3 + O_3 \longrightarrow \underset{\text{(Molozonide)}}{CH_3\overset{O-O-O}{CH-CH}CH_3} \longrightarrow CH_3CHO + \dot{O}O\text{-}\dot{C}\begin{matrix} / H \\ \backslash CH_3 \end{matrix} \qquad (4\text{-}11)$$

The biradical formed in this process can undergo a number of reactions. It can thermally decompose to yield a variety of free-radical intermediates or it can react with a number of species, including NO, NO_2, SO_2, H_2O, and aldehydes (Su et al., 1980; Niki et al., 1981; Dodge and Arnts, 1978).

Knowledge about the reactions of the aromatic compounds in the atmosphere is not nearly as complete as knowledge about the reactions of alkanes and alkenes. Although aromatics comprise between 20 and 30 percent of the VOC carbon in urban atmospheres, the reaction intermediates and final reaction products of the aromatics are not well known. Different research groups (Killus and Whitten, 1982; Atkinson et al., 1980) have constructed aromatic mechanisms that model, with a certain success, smog chamber systems containing aromatics and NO_x. This is not to say that these mechanisms accurately describe the chemistry involved, but that within the bounds of uncertainty that exist in the reactions, their products, and associated rate constants, these models can be "tuned" to predict NO, NO_2, and O_3 behavior. Much additional work, however, is needed to describe the chemical processes that take place.

Laboratory studies show that under ambient conditions, HO· attack on aromatics is initially the primary path of reaction (Hendry et al., 1978; Atkinson et al., 1979). In terms of O_3 produced, their reactivity increases from benzene to toluene to the xylenes. The aromatic rings are cleaved (Killus and Whitten, 1982; Atkinson et al., 1980) and one of the end products of the reaction pathways is peroxyacetyl nitrate (PAN) (Darnall et al., 1979).

A noteworthy finding in the past 5 years is that some nitrogenated products of the photochemical smog system, such as PAN and possibly peroxynitric acid ($HOONO_2$) (Kamens et al., 1981), have a greater mechanistic role than thought earlier. Previous investigations of PAN chemistry (Pate et al., 1976; Cox and Roffey, 1977; Hendry and Kenley, 1977) had shown that PAN can thermally decompose to a peroxyacyl radical and NO_2 and that the rate of decomposition is extremely temperature-dependent. Therefore, significant levels of PAN can build up early in the day when temperatures are relatively low. In the late afternoon, when ambient temperatures are higher, the decomposition of PAN can proceed at a rapid rate, liberating NO_2 molecules that can lead to enhanced O_3 production. Despite, however, the tendency toward thermal decomposition at afternoon temperatures, the rate of formation of PAN may be so high in the afternoon that PAN concentrations may reach their peak at that time (Tuazon et al., 1981).

The natural hydrocarbons, i.e., organic compounds emitted from vegetation, can also react with NO_x in the presence of sunlight to form O_3, and perhaps other oxidants. On a global basis, the quantities of natural hydrocarbons emitted are higher than those from manmade sources (section 3.4.2). Their concentrations in ambient air are much lower, however, especially in the vicinity of urban areas (sections 3.4.2 and 3.5). More important, recent reports (Arnts and Gay, 1979; Arnts et al., 1981; Roberts et al., 1983) continue to confirm that natural hydrocarbons play the dual role of ozone precursor and ozone scavenger and that the latter role seems to be the more important one. Thus, natural hydrocarbons are not thought to contribute much ozone or other oxidants to urban environments. The contribution of natural hydrocarbons to the formation of ozone generally and the contribution to urban ozone specifically remain areas of debate. The published literature on the role of natural hydrocarbons has recently been critically reviewed by Altshuller (1983).

4.2.5 Relationship of Ozone to Aerosol-Related Phenomena

In addition to having direct adverse effects on human health and on vegetation, ecosystems, and nonbiological materials, ozone can contribute indirectly to visibility degradation and to acidic deposition via its participation in the formation of both organic and inorganic aerosols (National

Academy of Sciences, 1977; U.S. Environmental Protection Agency, 1982a). It is well established that the source of the vast majority of manmade sulfate aerosol in the atmosphere is the oxidation of sulfur dioxide (SO_2), ultimately to sulfuric acid (H_2SO_4). The correlations between elevated levels of ozone and of sulfate aerosol in ambient air have been noted by several investigators in field studies concerned with visibility reduction by aerosols. Wilson (1978) and Gillani et al. (1981) have pointed out that atmospheric mixing intensity and the background O_3 concentration are the two most important factors in determining SO_2 oxidation at relative humidities lower than 75 percent. It is also clear, however, that the rate of reaction of O_3 with SO_2 is far too slow to account for observed formation rates of sulfate aerosol (U.S. Environmental Protection Agency, 1982a).

Of the many possible gas-phase reactions of SO_2, only a few appear to have any significance in the production of sulfate aerosol. The reaction of HO· with SO_2 appears to be the dominant pathway for the oxidation of SO_2 (Calvert and Stockwell, 1983; Calvert and Mohnen, 1983). A recent analysis by Stockwell and Calvert (1983) implicates the formation of $HOSO_2$ radicals from the reaction of HO· with SO_2, followed by reaction with O_2, as the favored mechanism for the formation of SO_3:

$$HO\cdot + SO_2\ (+\ M) \longrightarrow HOSO_2\cdot\ (+\ M); \qquad (4\text{-}12)$$

$$HOSO_2\cdot + O_2 \longrightarrow HO_2\cdot + SO_3. \qquad (4\text{-}13)$$

From the reaction of $HO_2\cdot$ with NO, HO· is regenerated:

$$HO_2\cdot + NO \longrightarrow HO\cdot + NO_2\cdot \qquad (4\text{-}14)$$

and the cycle begins again (see equation 4-9, section 4.2.1). The importance of the reaction of HO· with SO_2 in the atmosphere is supported by observations of power plant plumes, in which no aerosol is formed at night when the HO· concentration in the ambient air is negligible; and none is formed during the day before the plume is well mixed with ambient air (the ambient air contains much higher concentrations of HO· and O_3 than the plume) (Blumenthal et al., 1981; Davis et al., 1979).

In addition to sources of HO· already discussed (equation 4-11 and the photolysis of HONO), the photolysis of O_3, in relatively clean background air, and the subsequent reaction of the liberated oxygen atom with a water molecule provide an important source of HO· radicals for the SO_2 oxidation (Hegg and Hobbs, 1980). Similarly, the reaction of O_3 with olefins in polluted air leads to the formation of HO· radicals. One can therefore conclude that O_3, though it does not react directly with SO_2 at an appreciable rate, plays an important indirect role in the transformation of SO_2 to sulfate aerosol via homogeneous oxidation of SO_2 in both clean and polluted atmospheric systems. That contribution can not be quantified, however, at least at present (U.S. Environmental Protection Agency, 1982a).

Despite the poor quality of the available data, the possibility that nitrate aerosol is a contributor to visibility reduction should not be neglected. The role of O_3 in the formation of this aerosol species is briefly considered here. The principal manmade nitrogen emissions of interest here are NO and NO_2, the vast majority of which are NO. This species is relatively insoluble in water (section 3.2) and does not react with water in any significant manner. Thus, NO must be converted to some more highly oxidized form in order to participate in the formation of particulate nitrate.

The oxidation of NO to NO_2 can occur through thermal oxidation at very high concentrations of NO such as those in and very near the stacks of power plants (U.S. Environmental Protection Agency, 1982b). This generates only a small portion of the NO_2 formed in the atmosphere, however. As explained earlier, the most important reactions leading to formation of NO_2 in ambient air are:

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (4\text{-}15)$$

$$NO + HO_2\cdot \longrightarrow NO_2 + HO\cdot \qquad (4\text{-}14)$$

Thus, if NO_2 is a precursor of nitrate aerosol, O_3 plays a significant direct role in its formation by oxidizing NO, and an indirect role by leading to formation of $HO_2\cdot$ radicals as discussed above. Following oxidation of NO, the NO_2 can be converted in the gas phase to nitric acid vapor through either of two pathways:

$$NO_2 + HO\cdot \longrightarrow HNO_3 \qquad (4\text{-}16)$$

or,

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \qquad (4\text{-}17)$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \qquad (4\text{-}18)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \qquad (4\text{-}19)$$

The first pathway, which is dominant during the daytime, requires the presence of HO· radicals that are produced during the formation of O_3, as well as from other sources. The second pathway to HNO_3 is dominant at night and directly involves reaction with O_3.

Nitric acid (HNO_3), once it has been produced in the gas phase, is sufficiently volatile to remain in the atmosphere as a vapor. The available laboratory and ambient air data indicate, however, that HNO_3 vapor reacts with ammonia to form NH_4NO_3 (Appel et al., 1980; Doyle et al., 1979; Stelson et al., 1979), which, because of its low vapor pressure, will form nitrate aerosol particles. Evidence also indicates that HNO_3 vapor will react with NaCl aerosol in the following way:

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3 \qquad (4\text{-}20)$$

$$HNO_3 + NaCl \longrightarrow NaNO_3 + HCl \qquad (4\text{-}21)$$

This second reaction (equation 4-21) may account for the fact that much of the observed particulate nitrate in Los Angeles is found in the coarse mode (Farber et al., 1982). Obviously, the importance of this mechanism for nitrate aerosol formation is determined by the availability of sea salt particles.

Sulfate and nitrate aerosols are present at significant levels in the atmosphere in the form of just a few compounds. In contrast, secondary organic aerosols are composed of a large number of species, but there is no clear consensus concerning which ones contribute most to the mass concentration. For all the species that are found in the secondary organic aerosol, however, the fundamental formation mechanism is the same (chapter 5). The vapor-phase precursor undergoes some reaction that results in formation of a product having an equilibrium vapor pressure sufficiently low that condensation, nucleation, or both are possible at the gaseous concentration achieved. From the available data, it seems clear that the more highly oxygenated, larger-carbon-number species generally are those precursors likely to form secondary aerosols in the atmosphere.

For an earlier but thorough review of the formation of secondary aerosol, the reader is referred to the 1977 monograph on ozone and other photochemical oxidants by the National Academy of Sciences (1977). Two recent criteria documents prepared by the U.S. Environmental Protection Agency (1982a; 1982b) contain thorough discussions of the contributions of ozone and of hydrogen peroxide, also an oxidant, to the oxidation of SO_2 and NO_2, as well as of the respective roles of SO_2 and NO_2 as precursors to visibility impairment and acidic deposition.

The reactions of manmade volatile organic compounds that produce aerosols were thoroughly reviewed and documented in the National Academy of Sciences monograph cited above. Biogenic as well as manmade volatile organic compounds, however, can participate in aerosol formation (Altshuller and Bufalini, 1971; Arnts and Gay, 1979). Direct experimental evidence of aerosol formation, however, along with product analysis is available for only a limited number of natural compounds, α-pinene and β-pinene (National Academy of Sciences, 1977; Hull, 1981; Schwartz, 1974), mainly because the analysis and characterization of these kinds of products at ambient concentrations is extremely difficult. Hull has conducted experiments with these two compounds at high concentrations in a small tube reactor. Analysis of the products showed, on a weight basis, that almost all of the reacted α-pinene carbon was found in the condensed material extracted from the walls. Although the products he identified from these experiments were either in the condensed phase or on the walls, Hull suggested that at the α-pinene levels found in ambient air these products have a high enough vapor pressure to exist both in the gas phase and in aerosols (Hull, 1981). In his recent review of the role of biogenic volatile organic compounds, Altshuller (1983) also discusses at length the contribution of these compounds to ambient air aerosols.

4.3 METEOROLOGICAL AND CLIMATOLOGICAL PROCESSES

As discussed in the previous section, ozone and oxidants are formed by the action of sunlight on the precursors, NO_2 and hydrocarbons. The accumulation of the products to form an appreciable concentration is also dependent, however, on the prevailing meteorology in the vicinity of the precursor emissions.

To understand the details of the effects of meteorology on air quality requires a thorough knowledge of meteorology and climatology, but an appreciation of the general factors important in the formation of elevated concentrations of oxidants is relatively easy to acquire. Following is a brief presentation of some features of atmospheric mixing and transport that will provide a basic understanding of the meteorological factors that affect the concentrations of ozone and other oxidants in urban and rural areas.

4.3.1 Atmospheric Mixing

The concentration of an air pollutant depends significantly on the degree of mixing that occurs between the time a pollutant or its precursors are emitted and the arrival of the pollutant at the receptor. Since, to a first approximation, the diurnal cycle of weekday urban emission patterns for ozone and oxidant precursor pollutants is generally uniform, it is reasonable to ascribe a significant proportion of the large day-to-day changes in pollutant concentrations to changes in meteorological mixing processes. The rate at which atmospheric mixing processes occur and the extent of the final dilution of the pollutants depends on the amount of turbulent mixing and on wind speed and wind direction. Moreover, the transport of pollutants and precursors from a source region to a distant receptor is also dependent on wind speed and wind direction.

The degree of turbulent mixing can be characterized by atmospheric stability. In an atmospheric layer with relatively low turbulence, pollutants do not spread as rapidly as they do in an unstable layer. Also, because a stable layer has a relatively low rate of mixing, pollutants in a lower layer will not mix through it to higher altitudes. The stable layer can act as a trap for air pollutants lying beneath it. Hence, an elevated inversion is often referred to as a "trapping" inversion. Also, if pollutants are emitted into a stable layer aloft, such as from a stack, the lack of turbulence will keep the effluents from reaching the ground while the inversion persists.

It is common in air pollution considerations to equate a stable atmospheric layer or situation with a temperature inversion, which is a layer of the atmosphere in which the temperature increases with increasing altitude, because inversions are common and also represent the most stable atmospheric situations. The lowest part of an inversion layer is called the base and is defined as the altitude at which the temperature begins to increase. The top of the inversion is the point at which the temperature begins to decrease with increasing altitude. The distance between the base and top of the inversion layer is the "depth" or "thickness" of the inversion. Inversion layers may begin at the ground surface (i.e., the altitude of the base is zero), or the entire inversion layer may be above the surface. The former is known as a "surface inversion" and the latter as an "elevated inversion." The two types are usually caused by different sets of weather conditions, but it is not unusual for both types of inversions to be present at a given location at the same time. In the United States, surface inversions are characteristic of nighttime and early morning hours except when heavy cloud cover or windy and stormy conditions prevail.

Surface and elevated inversion layers are both important in determining pollutant concentration patterns since, as noted above, mixing and dilution processes proceed at a relatively slow rate in such layers. Thus, if pollutants are emitted into an inversion layer, relatively high concentrations can persist for a considerable period of time or over a considerable distance of wind travel from the source. For example, a surface inversion in the morning could cause automotive exhaust pollutants released at the surface during the morning rush hours to persist with minimum dilution near the ground surface for an extended period of time, probably for 1 or 2 hours after sunrise, until solar radiation heats the ground and causes the inversion to disappear or "break" (Hosler, 1961; Slade, 1968). High concentrations may occur at the ground even when an elevated inversion is present and the layers below the inversion are unstable and are undergoing good mixing. Such a persistent elevated inversion layer is a major meteorological factor that contributes to high pollutant concentrations and photochemical smog situations along the southern California coast (Holzworth, 1964; Hosler, 1961; Robinson, 1952).

The vertical mixing profile through the lower layers of the atmosphere follows a typical and predictable cycle on a generally clear day. In such a situation a surface inversion would be expected to form during the early morning and to persist until surface heating becomes significant, probably 2 or 3 hours after sunrise. Pollutants initially trapped in the surface inversion may cause relatively high, local concentrations, but these concentrations will decrease rapidly when the surface inversion is broken by surface heating, usually about midmorning. The surface inversion will begin to form again during the early evening hours and pollutants from near-surface sources such as automobiles will experience progressively less dilution as the surface inversion develops.

Elevated inversions, when the base is above the ground, are also common occurrences (Hosler, 1961; Holzworth, 1964). Since these conditions, however, are identified with specific synoptic conditions, they are much less frequent than the nighttime radiation inversion. Because it may persist throughout the day and thus restrict vertical mixing, an elevated inversion is nevertheless a very significant air pollution feature. Smog-plagued southern California is adversely affected by persistent elevated inversions (Robinson, 1952). When compared to a source near the surface and the effects of a radiation (surface) inversion, the pollutant dispersion pattern is quite different for an elevated source plume trapped in a layer near the base of an elevated inversion. This plume will not be in contact with the ground surface in the early morning hours because there is no mixing downward through the surface radiation inversion. Thus, the elevated plume will not affect surface pollutant concentrations until the mixing processes become strong enough to reach the altitude of the plume. At this time, the plume may be mixed downward quite rapidly in a process called "fumigation." After this initial mixing, surface concentrations will decrease as the usual daytime mixing processes continue to develop. If the daytime mixing becomes strong enough to break the upper inversion, the pollutants may be mixed through an increasingly deep layer of the atmosphere. When surface heating decreases in the late afternoon and early evening, both the surface and elevated inversions will form again. The surface inversion will again prevent pollutants from elevated sources from reaching the ground and surface scavenging processes will gradually reduce the concentrations of pollutants trapped during the formation of the surface inversion.

Geography can have a significant impact on dispersion of pollutants (e.g., along the coast of an ocean or one of the Great Lakes). Near the coast or shore, the temperatures of land and water masses can be different, as can the temperature of the air above such land and water masses. When the water is warmer than the land, there is a tendency toward reduction in the frequency of surface inversion conditions inland over a relatively narrow coastal strip (Hosler, 1961). This in turn tends to increase pollutant dispersion in such areas. Such conditions may occur frequently on the Gulf Coast. The opposite condition also occurs if the water is cooler than the land, as in summer or fall. Cool air near the water surface will tend to increase the stability of the boundary layer in the coastal zone, and thus decrease the mixing processes that act on pollutant emissions. These conditions occur frequently along the New England coast (Hosler, 1961). Similarly, pollutants from the Chicago area have been observed repeatedly to be influenced by a stable boundary layer over Lake Michigan (Lyons and Olsson, 1972). This has been observed especially in summer and fall when the lake surface is most likely to be cooler than the air that is carried over it from the adjacent land.

Since the diurnal mixing conditions are such an important part of the meteorological parameters for understanding pollutant mixing and diffusion, it is useful to have some knowledge of the mixing cycles that prevail over the United States. Figures 4-2 and 4-3 show the average summer morning and afternoon mixing heights as calculated on the basis of upper air temperature data and an estimated midmorning urban temperature. Since Holzworth (1972) attempted to include the influence of an urban heat island in this estimated temperature, the morning results in Figure 4-2 are probably most applicable to larger urban areas. Rural or nonurban areas would be expected to have lower mixing heights.

Summer conditions are useful to consider because of the prevalence of high photochemical oxidant concentrations during this season. As shown in Figure 4-2, morning mixing heights are estimated to be greater than 300 meters except for the central part of the Great Basin, where a 200-meter isopleth includes parts of Oregon, Idaho, Utah, Arizona, and most of Nevada. By midafternoon (Figure 4-3), the estimated mixing height at the time of maximum temperature has increased markedly, and only a few coastal areas have an average afternoon maximum mixing height of less than 1000 meters. In contrast to the morning data, the central Great Basin area becomes the area of greatest mixing in the afternoon. This would be expected since this is a hot, arid, desert region, and the driving force generating the surface mixing layer is the solar heating of the ground surface.

The magnitude of the afternoon mixing height is generally an indication of the potential for recurring urban air pollution problems. If a trapping, elevated inversion does not rise high enough in the afternoon to release the generated pollutants that are trapped, an accumulating episode is likely. From the average summer afternoon data shown in Figure 4-3, where the lowest average mixing height is 600 meters and almost all of the area has a value greater than 1500 meters, it would appear that urban air pollution should not be severe. On the average this is probably correct; however, there are several

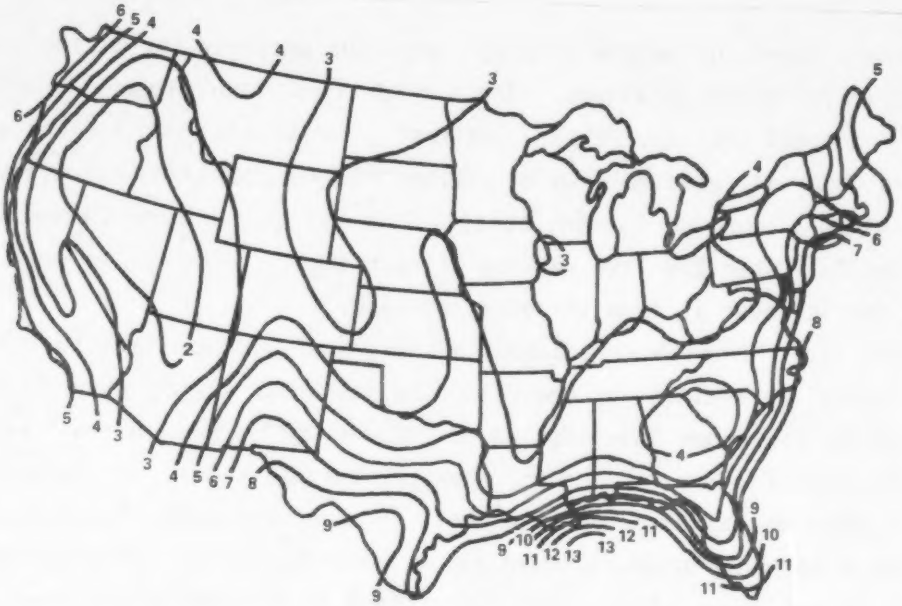

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Figure 4-2. Isopleths (m x 10^2) of mean summer morning mixing heights.

Source: Holzworth (1972).

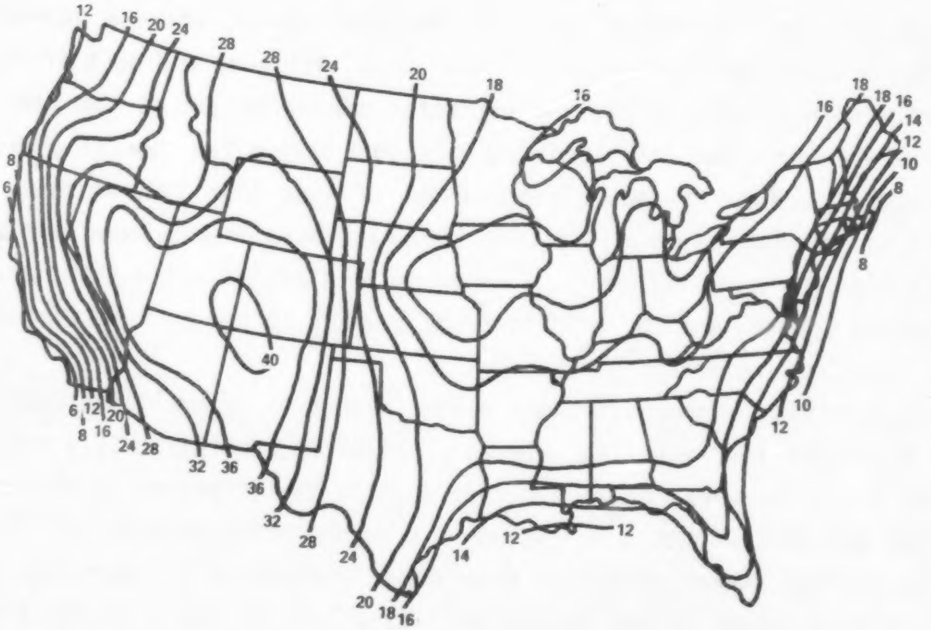
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Figure 4-3. Isopleths (m x 10^2) of mean summer afternoon mixing heights.

Source: Holzworth (1972).

departures from the average, which result in relatively low mixing heights and adverse dispersion over many areas of the United States on a recurring basis.

Figure 4-4 (Holzworth and Fisher, 1979) shows the frequency of occurrence of elevated inversions in summer having a base between 1 and 500 meters (1600 feet) at the time of the afternoon upper air temperature measurement, 6:10 p.m. EST or 3:15 p.m. PST. The California coastal conditions, in which low inversions occur with a frequency of nearly 90 percent, are clearly evident. The northeastern coastal area from New Jersey north to Maine, where cool ocean water prevails, also has a relatively high percentage, above 20 percent, compared to most of the rest of the country. Stations bordering one of the Great Lakes--Green Bay, Sault St. Marie, and Buffalo--reflect a stabilizing lake effect with percentages above 5 percent. Except along the Pacific Coast, these ocean and lake coastal situations are probably limited to relatively narrow coastal zones (Hosler, 1961). Examples are evident in Figure 4-4, in which it may be noted that inversion frequencies of 21 to 28 percent occur in coastal New England compared to only 2 percent at Albany in upstate New York. A similar situation is evident in a comparison of the 3 percent inversion frequency at Washington, D.C., with the 16 percent frequency on the Delaware coast. A non-coastal region having summer afternoon low-level elevated inversions more than 5 percent of the time is the Southeast, where an area from Louisiana and Arkansas to the Atlantic coast shows frequency values between 5 and 10 percent. Other seasons differ in details, but the general patterns are similar.

This means that, for most of the United States, low-level stable layers that persist through the afternoon hours are rare events, occurring on less than 1 day in 20. Thus, air pollution situations in areas such as Kansas or Iowa will be related to the periods when the expected morning surface inversion persists later in the morning than usual and when winds are not strong enough to carry pollutants rapidly away from the local area. Along both the Pacific Coast and the Northeast Coast, low-level afternoon inversions are frequent enough to be a significant contributor to local and regional air pollution episodes.

4.3.2 Wind Speed and Mixing

Another major meteorological factor in the urban pollutant dispersion problem is low-level or surface-layer wind. As would be expected, strong

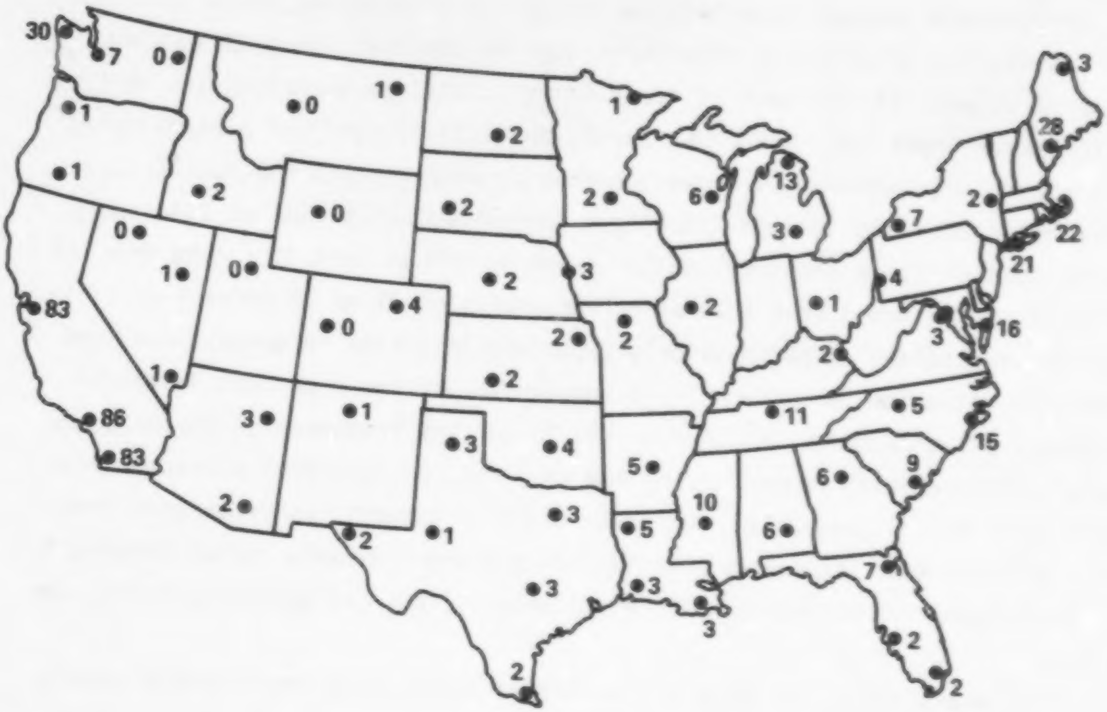
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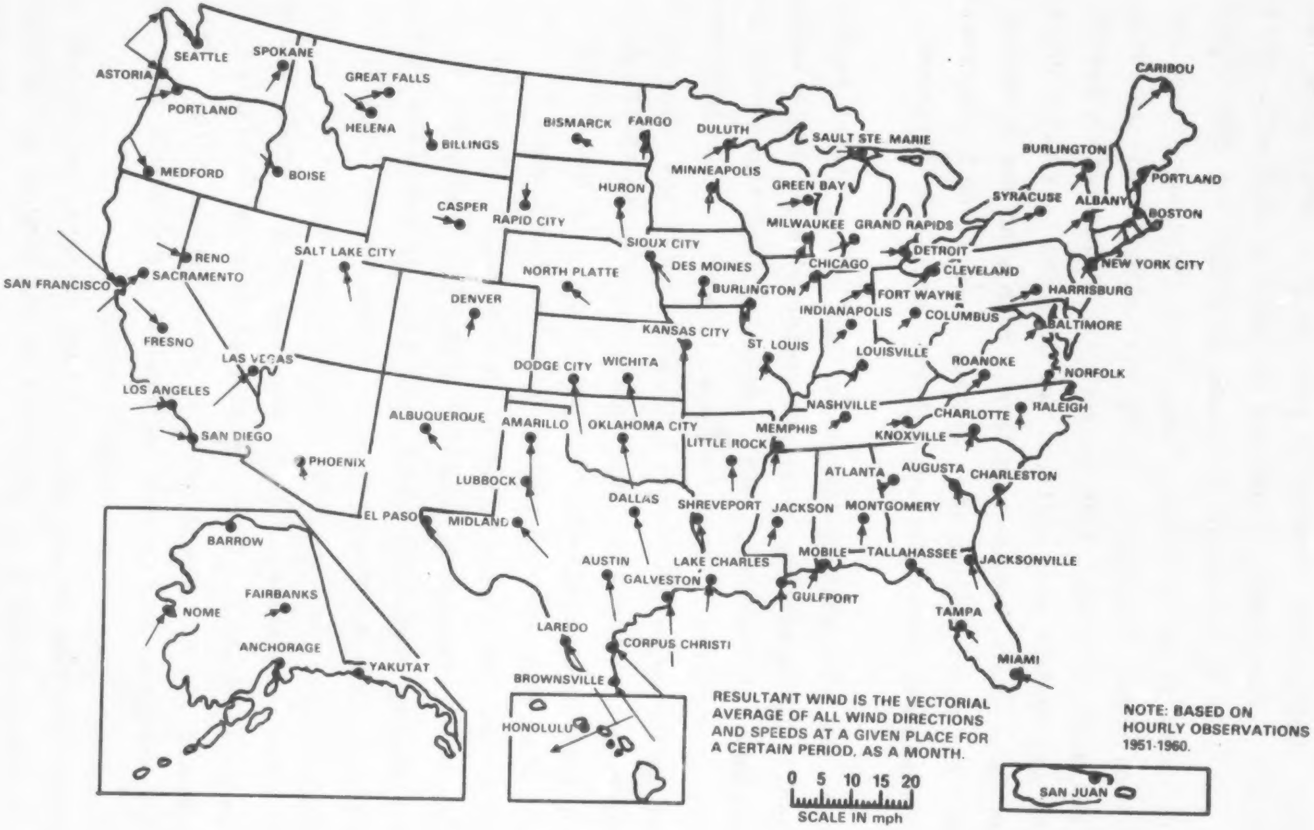
Figure 4-4. Percentage of summer 2315 GMT (6:15 PM EST, 3:15 PM PST) soundings with an elevated inversion base between 1 and 500 m above ground level.

Source: Adapted from Holzworth and Fisher (1979).

winds across a source area will dilute pollutant concentrations even though there is a strong, low-level inversion base. San Francisco is one example of such a location where strong winds frequently provide good ventilation in spite of a low inversion. Conversely, light and variable or calm wind conditions over an area can lead to excessive pollutant accumulations even though the afternoon mixing depth is quite large. Thus, it is necessary to include wind direction and wind speed frequencies in any evaluation of air pollution potential for a given area. It must also be recognized that both elevated inversion conditions and surface wind patterns are governed to a major degree by the synoptic, or large-scale, weather patterns. Both wind and inversion factors tend to favor pollutant buildup when a deep, slow-moving high-pressure system dominates the weather across an area (Korshover, 1967; Korshover, 1975).

Figure 4-5 shows the wind climatology across the United States in the month of July by depicting the monthly resultant vector wind at major weather stations (U.S. Department of Commerce, 1968). Note that the flow across the West Coast is generally directed inland, from west to east. This contributes to a typical situation for major California cities: significant urban pollutant plumes are found east of the urban core source areas while the immediate coastline or beach areas are relatively pollutant-free. In the Northeast States, the average wind flow is from southwest to northeast more or less parallel to the coastline. As a result, pollutant plumes from the major urban areas along this coast are frequently additive along the trajectory of the wind. Polluted air moving toward the coast from major inland urban sources may also be a factor in this Northeast region. Along the Gulf Coast, the average winds form southerly, onshore flow. Under some weather situations, however, there is often an offshore flow in one area (e.g., Texas) and an onshore flow in an adjacent area. Thus, because of this recirculation, the onshore Gulf air masses are not always pollutant-free (Price, 1976). Before the situation was examined carefully, the recirculating pollutants were sometimes confused with natural background concentrations.

Wind climatology provides an average wind flow pattern, but it does not provide a complete assessment of the influences of the wind on air pollution dispersion. Wind speed and, in particular, the frequency of weak winds are an important aspect to be considered. Figure 4-6, adapted from Holzworth and Fisher (1979), shows the frequency with which early morning (6:15 a.m. EST or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RESULTANT WIND IS THE VECTORIAL AVERAGE OF ALL WIND DIRECTIONS AND SPEEDS AT A GIVEN PLACE FOR A CERTAIN PERIOD, AS A MONTH.

NOTE: BASED ON HOURLY OBSERVATIONS 1951-1960.

Figure 4-5. Mean resultant surface wind pattern for the United States for July. Direction and length of arrows indicate monthly resultant wind.

Source: U.S. Dept. of Commerce (1968).

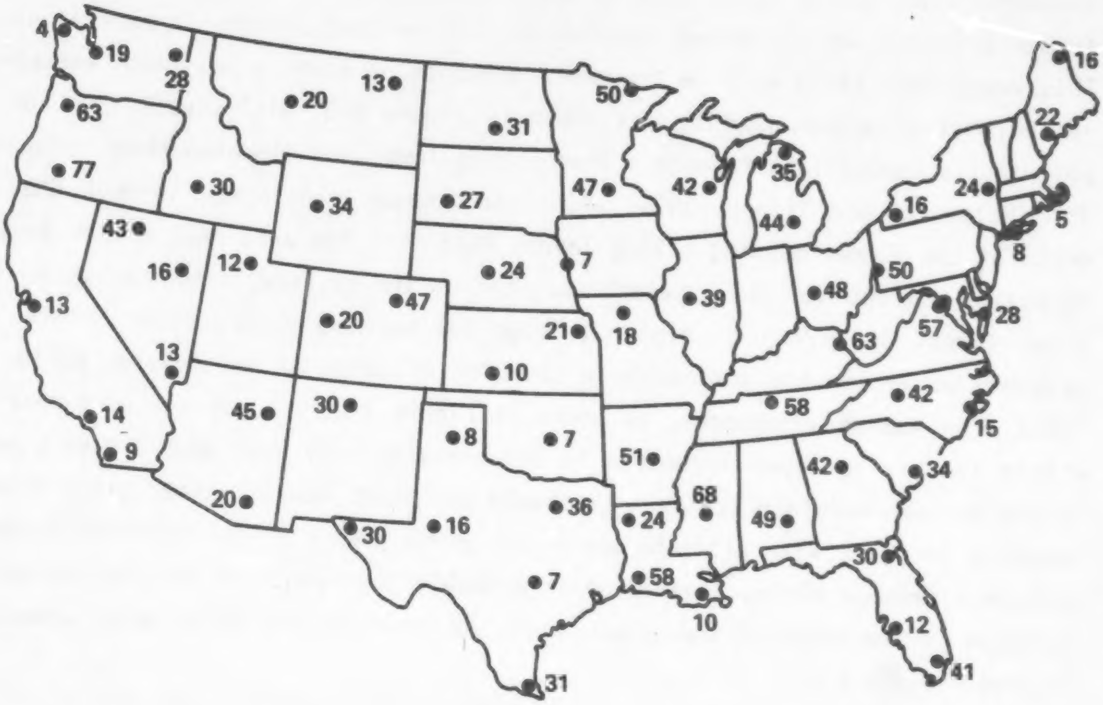
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Figure 4-6. Percentage of summer 1115 GMT (6:15 AM EST, 3:15 AM PST) soundings with an inversion base at the surface and wind speeds at the surface ≤2.5 m/sec.

Source: Adapted from Holzworth and Fisher (1979).

3:15 a.m. PST) surface inversions occur with calm or weak surface winds; that is, wind speeds equal to or less than 2.5 m/sec or 6 mi/hr. There is considerable variation between stations because terrain and geography (e.g., coastal locations) influence both the wind flow and inversion frequency. It is clear, however, that over large areas of the United States, especially in heavily industrialized inland areas east of the Mississippi River, calm amd stable summer mornings are a frequent occurrence: 50 percent or more in many areas. This means that there will be frequent incidents of morning pollutant accumulation; but afternoon heating, as shown by Figure 4-3, will usually mix the pollutant accumulations through a deep mixing layer and disperse them. Figure 4-7 (Holzworth and Fisher, 1979) shows the average wind speed through the depth of the summer morning mixing layer. Note that the area east of the Rocky Mountains, except for the Appalachians, can on the average, expect winds of 4 m/sec (about 10 mi/hr) or higher through the morning mixing layer. This probably would provide acceptable midmorning dilution of accumulated pollutants. In summer afternoons, as shown in Figure 4-8, the average wind speed within the mixing layer increases in all areas and may even double over some of the western mountain states. It should be noted, however, that since winds normally increase with altitude above the ground, much of the increase in the average afternoon mixing layer wind is probably the result of the considerable increase in the depth of the mixed layer, as shown by the differences between Figures 4-2 and 4-3.

In summary, atmospheric mixing parameters of stability and wind in the pollutant transport layers can exert controlling effects on O_3 and oxidant concentrations. The effects include the amount of dilution occurring in the source area, as well as along the trajectory followed by an urban or source-area plume. Regions having steady prevailing winds, such that a given air parcel can pass over a number of significant source areas, can develop significant levels of pollutants even in the absence of weather patterns that lead to the stagnation type of air pollution episodes. The Northeast states are highly susceptible to pollutant plume transport effects, although some notable stagnation episodes have also affected this area (e.g., Lynn et al., 1964). Along the Pacific Coast, especially along the coast of California, coastal winds and a persistent low inversion layer contribute to major pollutant buildups in urban source areas and downwind along the urban plume trajectory (Robinson, 1952; Neiburger et al., 1961). In the southern Appalachians, the

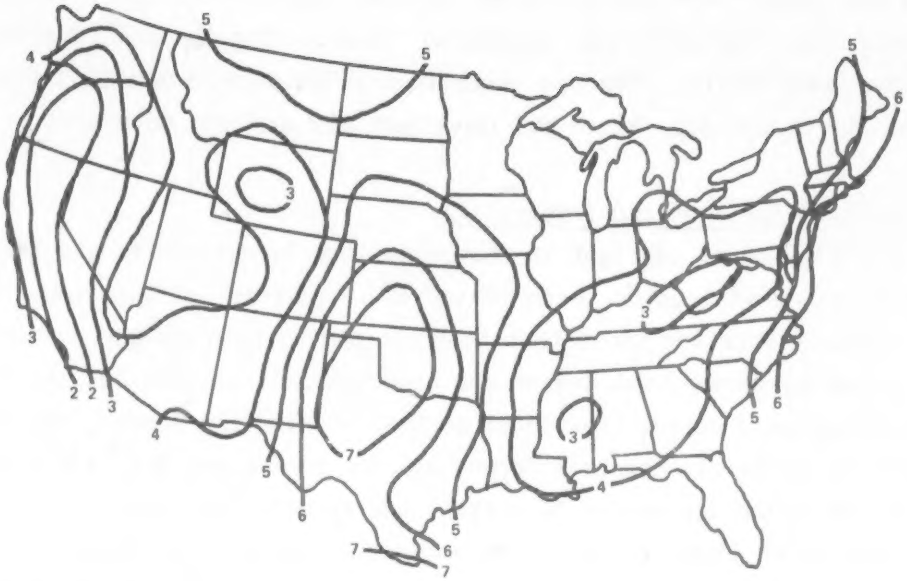
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Figure 4-7. Isopleths (m/sec) of mean summer wind speed averaged through the morning mixing layer.

Source: Holzworth and Fisher (1972).

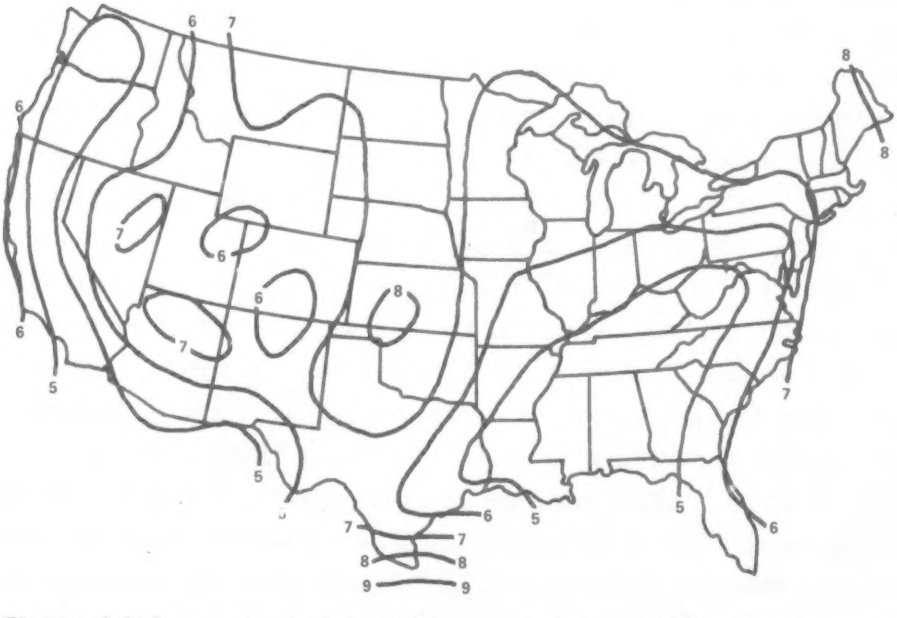
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Figure 4-8. Isopleths (m/sec) of mean summer wind speed averaged through the afternoon mixing layer.

Source: Holzworth and Fisher (1972).

weather favors longer-term air pollution episodes (Korshover, 1967; Korshover, 1975). Generally, low pollution potential results from the conditions that occur in the Great Plains area and south to the Texas-Louisiana Gulf Coast; and between the Mississippi River and the crest of the Rocky Mountains.

4.3.3 Effects of Sunlight and Temperature

The significance of sunlight in photochemistry is related to its intensity and its spectral distribution, both of which have direct effects upon the specific chemical reaction steps that initiate and sustain oxidant formation. Sunlight intensity varies with season and geographical latitude but the latter effect is strong only during the winter months. During the summer, the maximum light intensity is fairly constant throughout the contiguous U.S. and only the duration of the solar day varies to a small degree with latitude.

The effects of light intensity on individual photolytic reaction steps and on the overall process of oxidant formation have been studied in the laboratory (Peterson, 1976; Demerjian et al., 1980). All of the early studies, however, employed constant light intensities, in contrast to the diurnally varying intensities that occur in the ambient atmosphere. More recently, diurnal variation of light intensity has been recognized and studied as a factor in photochemical oxidant formation (Jeffries et al., 1975; Jeffries et al., 1976). Such studies showed that the effect of this factor varies with initial reactant concentrations. Most important was the observation that similar NMOC/NO_x systems showed different oxidant potential depending on whether studies of these were conducted using constant or diurnal light. This has led to incorporation of the effects of diurnal or variable light into photochemical models (Tilden and Seinfeld, 1982).

While the effect of sunlight intensity is direct and has been amply demonstrated (Leighton, 1961; Winer et al., 1979), the effect of wavelength distribution on the overall oxidant formation process is subtle. Experimental studies have shown the photolysis of aldehydes to be strongly dependent on radiation wavelength in the near UV region (Leighton, 1961); and there is some indication (Bass et al., 1980) that the photolysis rates for aldehydes may be temperature-dependent. Since aldehydes are major products in the atmospheric photooxidation of NMOC/NO_x mixtures, it is inferred that the radiation wavelength should have an effect on the overall photooxidation process. This inference was directly verified, at least for the propylene/NO_x and n-butane/NO_x chemical systems, in smog chamber studies (Jaffee et al., 1974; Winer et al., 1979). In the ambient atmosphere, some variation in the wavelength distribution of sunlight does occur as a result of variations in time of day, stratospheric O_3, ambient aerosol (Stair, 1961), and cloud cover.

It has been observed that days on which significant ozone-oxidant concentrations occur are usually days with warm, above-normal temperatures (Bach, 1975). This temperature effect can be explained readily as a synoptic meteorological correlation rather than as a temperature-photochemical rate constant effect, in that periods of clear skies and warm temperatures are periods of high air pollution potential, as discussed above. Because of the close correlation between above-normal temperatures and high air pollution potential, a maximum daily temperature forecasting procedure is often useful as a substitute for a more elaborate and specific program for forecasting air pollution potential. The correlation between temperature and, thus, synoptic weather conditions and photochemical air pollution intensity has been observed in a number of areas. Evaluation of photochemical air pollution in Los Angeles as early as 1948 showed a correlation with temperature. Recent studies of O_3 patterns in St. Louis, Missouri, have also shown a correspondence between daily maximum O_3 concentration and temperature (Shreffler and Evans, 1982).

4.3.4 Transport of Ozone and Other Oxidants and Their Precursors

The 1978 air quality criteria document for ozone and other photochemical oxidants made a convincing case for the fact that ozone and other photochemical oxidants are transported from urban source areas to downwind regions in concentrations approaching 0.1 ppm or more (U.S. Environmental Protection Agency, 1978a). This was a significant advance in the understanding of photochemical air pollution. It served to answer a number of perplexing problems that had been identified previously in studies of ozone and other photochemical oxidants in nonurban areas. These included high ozone or total oxidant concentrations in areas remote from identifiable sources. The 1978 criteria document also pointed out that the evaluation of impacts on local ozone or total oxidant concentrations resulting from transport into the area was still only a qualitative assessment and could not then be quantified.

There have been several recent extensive studies on oxidant transport for model development and on field measurements of oxidants for model verification. One such program was the Northeast Regional Oxidant Study (NEROS), which was carried out in 1979 and 1980 in the corridor from Washington, D.C., to Boston (Clarke et al., 1982). Reactive pollutant modeling for urban areas, particularly the Empirical Kinetic Modeling Approach (U.S. Environmental Protection Agency, 1981), has progressed rapidly in recent years.

Studies of the transport of ozone and other photochemical oxidants (O_3-O_x) are classified into three regimes, depending upon transport distance (U.S. Environmental Protection Agency, 1978). In the first, urban-scale transport, the occurrence of transport of photochemical pollutants can be detected in most large urban areas if there is sufficient O_3-O_x monitoring information. It has been identified as a significant, characteristic feature of the O_3-O_x problem in the Los Angeles basin (Tiao et al., 1975), as well as in San Francisco, New York, Houston, Phoenix, and St. Louis (Altshuller, 1975; Coffey and Stasiuk, 1975; Shreffler and Evans, 1982). Urban-scale transport patterns result from one or more of a combination of factors. First is the simple advection of the photochemically reacting air mass and the development of maximum O_3-O_x after 1 or 2 hours of downwind travel. Maximum concentrations may be displaced up to 20 or so miles from the center of the major source area. It has also been noted (U.S. Environmental Protection Agency, 1978a) that pollutant concentrations in air parcels in the central core area of major source areas may not be the most conducive for O_3-O_x formation because of the tendency toward occurrence there of more effective scavenging, especially scavenging related to NO and its reactions.

The distance of the peak O_3-O_x concentrations from the urban core area is dependent on the local wind pattern and is, in general, inversely related to the peak O_3-O_x concentration. Stronger winds will carry the air parcels farther during the reaction period, increasingly diluting pollutant concentrations along the trajectory. Weak winds and very restricted mixing heights will tend to cause higher O_3-O_x concentrations closer to the central source area. The diurnal wind cycle will also be an important factor, since in some situations calm conditions may prevail until late in the morning but in others a steady wind may be present throughout the emission and reaction process.

The second, or mesoscale, kind of transport of O_3-O_x is in many respects an extension of the urban-scale transport and is characterized by urban plume development. A report by Bell (1960) described November 1959 O_3-O_x incidents in northern coastal San Diego County, California. It showed conclusively that these were caused by the O_3-O_x and precursors formed and emitted, respectively, the previous day in the Los Angeles basin. The transport in these situations was over the coastal Pacific Ocean, and the O_3-O_x arrived at the San Diego receptor site as a contaminated sea breeze after overnight travel (Bell, 1960).

In the 1978 O_3-O_x criteria document, more than 30 references were cited relating to urban plume observations and investigations. Since 1978, the results of the 1975 New England oxidant study have been published in detail, and results of a more comprehensive 2-year field program carried out along the Washington, D.C.-Boston corridor in 1979 and 1980 have appeared in the literature (Clark and Clarke, 1982; Clarke et al., 1982; Vaughan et al., 1982). A major field program supported by local industries was conducted in Houston, Texas, although the O_3-O_x downwind plume phases were not as extensive as in NEROS. Chicago and adjacent shoreline areas of Lake Michigan have also been subject to a number of ground-level and airborne studies over distances of 150 to 300 kilometers (Lyons and Olsson, 1972; Sexton and Westberg, 1980; Sexton et al., 1981). As described above, O_3-O_x plumes from major urban areas can extend about 100 to 200 miles with widths of tens of miles (Sexton, 1982) and frequently up to half the length of the plume. Other field studies conclusively demonstrating mesoscale transport over New England have been reported (Spicer et al., 1979; Clarke et al., 1982; Cleveland et al., 1976a; Cleveland et al., 1976b; Rubino et al., 1976; Westberg et al., 1976; and Westberg et al., 1978). Although urban plumes are frequently thought of as a problem related only to large source areas such as New York and other major metropolitan areas, measurements in plumes from smaller urban areas have shown that these sources cannot be ignored (Sticksel et al., 1979; Sexton, 1982; and Spicer et al., 1982).

In the third kind of pollutant transport, synoptic-scale, the transport of O_3-O_x and precursors is characterized by the general and widespread elevated concentrations of pollutants that can occur on an air-mass scale under certain favorable weather patterns. These weather situations are generally slow-moving, well-developed high-pressure, or anti-cyclonic systems. This type of deep high-pressure area was considered by Korshover (1967, 1975) as a prerequisite for stagnating air pollution episodes. Not all high-pressure systems lead to high air pollution potential, however. Strong surface highs are frequently found in conjunction with well-developed low-pressure storm systems, resulting in brisk winds and good mixing, and, thus, low air pollution potential. Another type of high-pressure system, however, is one in which the surface high-pressure area is reinforced by a warm high-pressure circulation in the upper air. This is frequently characterized by weak winds, stable surface layers, and high pollution potential over regional or air-mass-sized areas. This is the meteorological pattern that is involved in synoptic-scale pollutant transport (Korshover, 1967; Korshover, 1975).

The importance of synoptic-scale or air-mass pollutant situations has been recognized for many years, probably much longer than the importance of major plumes has been apparent. The Donora, Pennsylvania smog episode in 1948 (Schrenk et al., 1949) involved the occurrence over a wide area of a regional air mass having relatively high pollution levels simultaneous with the occurrence of a stagnated warm high-pressure area over the Ohio Valley and the northern Appalachian area. Donora was an especially adversely affected pocket within this larger system.

The synoptic-scale high-pressure air pollution system is not characterized by well-defined urban plumes. Rather, a warm, slow-moving or stagnant anti-cyclone provides a synoptic-scale weather system that, because of weak winds and limited vertical mixing, favors the accumulation of relatively high concentrations of air pollutants. On a climatological basis, these systems are most common in the summer and fall months over most of the United States, as shown by the work of Korshover (1967; 1975). The general track of a system is from west or southwest to east or northeast. In many cases, an anti-cyclone will stagnate and intensify over the Midwest or East as circulation patterns in the upper air change and become more supportive of the surface anti-cyclonic pattern (Schrenk et al., 1949; Lynn et al., 1964).

Along the West Coast, air pollution problems are also the result of persistent high-pressure system influences. In this case, however, the high is the persistent subtropical anti-cyclone of the eastern Pacific rather than the series of transitory anti-cyclone systems characteristic of the area east of the Rocky Mountains. The persistent or semipermanent subtropical anti-cyclone in the Pacific is linked to the large-scale general circulation of the atmosphere rather than to moving wave systems (Neiburger et al., 1961). The effect is much the same, except that the area of limited mixing and more adverse air pollutant effects is found on the eastern edge of the subtropical anti-cyclone rather than the trailing western edge as in the transitory systems.

The identification and understanding of photochemical O_3-O_x and precursor transport by weather systems has provided a significant advance in understanding photochemical air pollution and the potential extent of its effects. Considerable progress has been made in the development of long-range photochemical modeling techniques so that the likely impact of synoptic systems can be anticipated. Such tools are very much in the research stage because the local impact of O_3-O_x results from a complex interaction of distant and local sources, urban plumes, mixing processes, atmospheric chemical reactions, and general meteorology.

4.3.5 Surface Scavenging in Relation to Transport

A major scavenging process for O_3 in the atmospheric boundary layer is adsorption and subsequent destruction at the ground surface. This occurs through the process of dry deposition, in which the process of eddy diffusion moves air parcels downward through the turbulent boundary layer to the laminar sub-layer. Individual molecules, such as ozone, will then move by Brownian motion through this laminar layer to the underlying surface. There reactive molecules, such as ozone, can be removed from the layer by reactions at the surface. These reactions can maintain a vertical concentration gradient, with the lowest concentrations occurring at the surface of the ground because of surface-scavenging reactions.

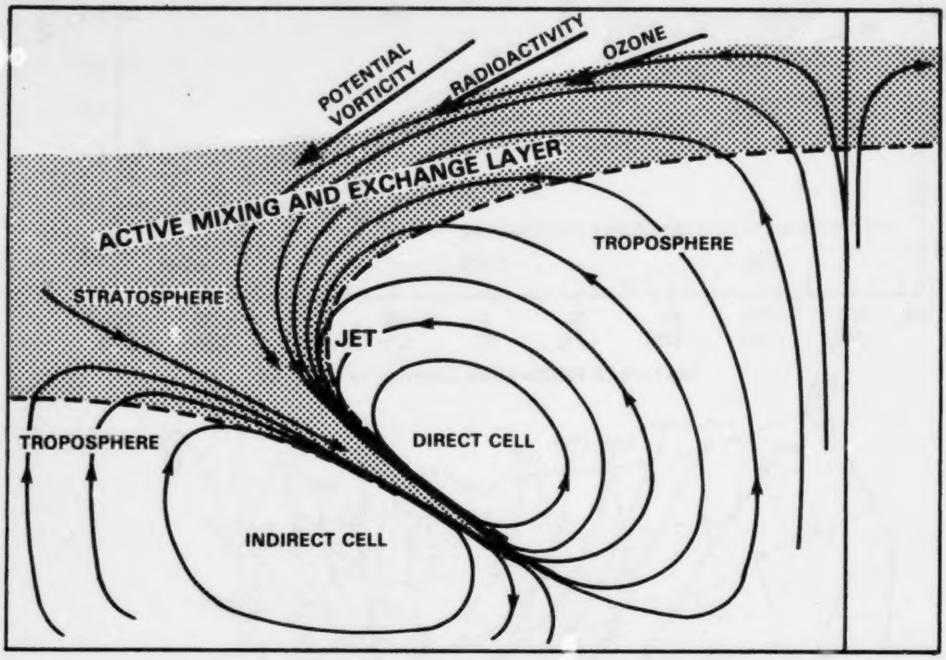
Because of this surface-scavenging process, ozone will persist in an atmospheric parcel in the absence of ozone-forming reactions only if the parcel is dispersed such that contact with the ground surface is minimized. It is likely that only in those air parcels moving above the surface layer will ozone escape the surface reactions and persist long enough to undergo long-distance transport. Aircraft observations have documented frequently the occurrence of relatively high ozone concentrations above lower-concentration surface layers. This is a clear indication that ozone is essentially preserved in layers above the surface and can be transported over relatively long distances when continual replenishment through precursor reactions is not a factor, such as at night.

4.3.6 Stratospheric-Tropospheric Ozone Exchange

The fact that O_3 is formed in the stratosphere, mixed downwa[illegible], and incorporated into the troposphere, where it forms a more or less uniformly mixed background concentration, has been known in various degrees of detail for many years (Junge, 1963). For example, one of the early questions resolved in studies of Los Angeles smog was to eliminate stratospheric ozone as a cause of the elevated ozone concentrations. For other areas and different sets of conditions, however, the importance of stratospheric ozone as a significant component of ground-level ozone cannot be ruled out.

The mechanisms by which stratospheric air is mixed into the troposphere have been examined by a number of authors. Danielsen conducted extensive analyses of major synoptic weather events that injected stratospheric air into the troposphere (Danielsen, 1968; Danielsen and Mohen, 1977; Danielsen, 1980). Reiter has been especially active in describing the atmospheric mechanisms by which stratospheric air injection takes place and in relating these processes to the global circulation of the atmosphere (Reiter, 1963; Reiter and Mahlman, 1965; Reiter, 1975). As a result of such research, exchange between the stratosphere and troposphere in the middle latitudes has been determined to occur to a major extent in events called "tropopause folds." In a tropopause fold (TF), the jet stream in the upper troposphere plays a major role in directing stratospheric air and high ozone concentrations into the troposphere. Figure 4-9 is a schematic presentation of the intrusion process as described by Danielsen (1968). The subsidence occurs along the poleward side of the polar jet stream in the area where the jet is associated with a cold front at ground level. The result is downward transport in the cold air behind the cold front.

Since 1978, a considerable amount of research on TF and ozone injection has been done, especially by SRI-International (Johnson and Viezee, 1981; Ludwig et al., 1977; Singh et al., 1980; and Viezee et al., 1979). Figure 4-10 from Johnson and Viezee (1981) shows one example of the probing by SRI of a TF event in the midwestern United States. Concentrations of ozone in excess of 90 ppb were found as low as 13,000 feet (3.9 kilometers), as shown in the upper part of Figure 4-10. These authors found that ozone intrusion was lower during this fall study (October 5, 1978) than in a number of other spring TF events. The dew point measurements in the second part of the figure confirm the stratospheric injection. The weather pattern accompanying this TF is shown at the bottom of Figure 4-10 by a 500 millibar (about 6 kilometer) chart; the surface cold front is also indicated. Note that the intrusion was detected well behind the cold front and appears to have assumed a layered formation in the altitude range of 8,000 to 12,000 feet (2.4 to 3.6 kilometers).


POTENTIAL VORTICITY
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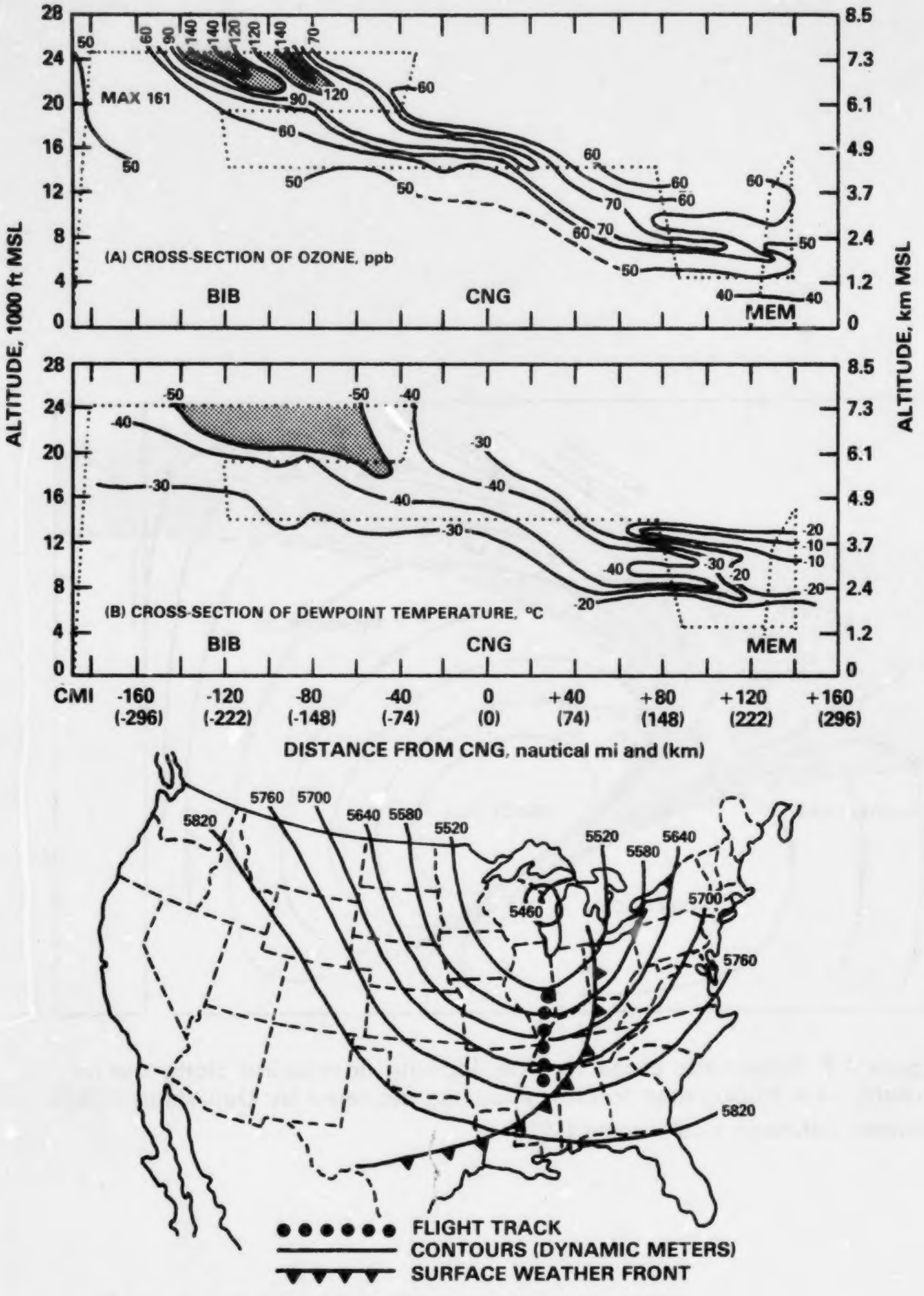
OZONE
ACTIVE MIXING AND EXCHANGE LAYER
TROPOSPHERE
STRATOSPHERE
JET
TROPOSPHERE
DIRECT CELL
INDIRECT CELL

Figure 4-9. Schematic cross section, looking downwind along the jet stream, of a tropopause folding event as modeled by Danielsen (1968). Source: Johnson and Viezee (1981).



(C) 500-mb CHART AND FLIGHT TRACK

Figure 4-10. Measured vertical cross-sections of (A) ozone, (B) dewpoint, and (C) the 500-mb chart and the flight track for October 5, 1978. CMI = Champaign, IL; CNG = Cunningham, KS; MEM = Memphis, TN.

Source: Johnson and Viezee (1981).

From their analysis of measurement flights in a number of TF situations, Johnson and Viezee (1981) concluded that the ozone-rich intrusion sloped downward toward the south. In terms of dimensions, the average crosswind width (north to south) at an altitude of 5.5 kilometers (18,000 feet) for six spring intrusions averaged 226 kilometers (746,000 feet), and for four fall TF systems, 129 kilometers (426,000 feet). Ozone concentrations at 5.5 kilometers (18,000 feet) averaged 108 ppb in the fall systemsand 83 ppb in the spring systems. Previously it had been assumed that only a few fairly intense systems would produce a TF event and trans-tropopause mixing. From their data, however, Johnson and Viezee (1981) drew the very important conclusion that all low-pressure trough systems, such as illustrated in Figure 4-10, may induce a TF event and cause the trans-tropopause movement of ozone-rich air into the troposphere.

On the basis of their field studies and the earlier models and work of Danielsen (1968), Johnson and Viezee (1981) proposed a set of model mechanisms or types of TF injection, which are illustrated in Figure 4-11 and described in the following general manner:

1. Type 1. The intrusion is broken up and dispersed by mixing and diffusion in the middle or free troposphere.
2. Type 2. The intrusion persists down to the planetary boundary layer or the top of the mixed layer, where the lower part of the intrusion may be incorporated into the mixed layer and may subsequently reach the ground.
3. Type 3. The intrusion occurs close behind the cold front, where the air parcels are caught by the downdrafts behind the cold front; and is brought to the ground by direct circulations associated with the front.
4. Type 4. The ozone-rich parcels are incorporated into convective cells and brought to the ground in association with rain-showers and thunderstorm downdrafts; similar to Type 3.

Johnson and Viezee (1981) summarize the possible impacts of these four types of TF events by noting that Types 1 and 2 should produce "relatively moderate effects" at the ground in comparison to those to be expected from Types 3 and 4. The latter two could cause "substantial" effects in terms of high surface ozone concentrations. The action of Types 3 and 4 are supported

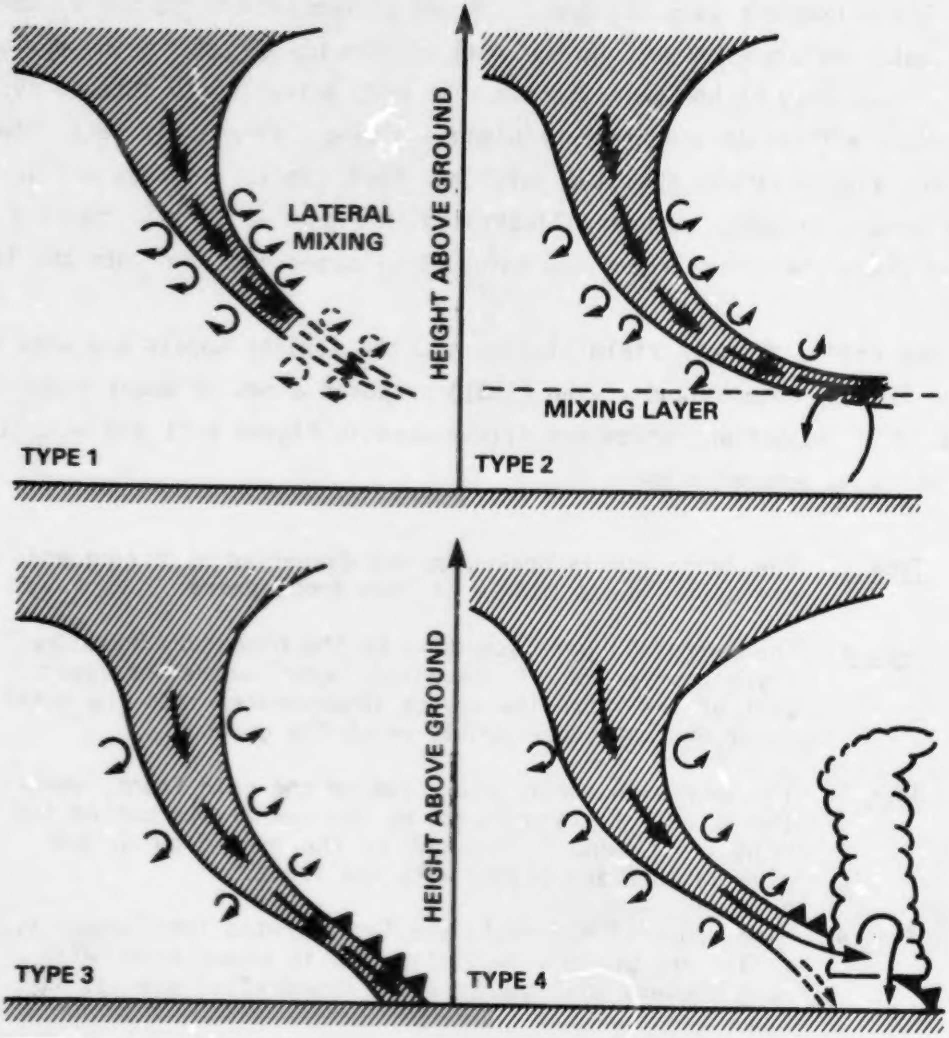

LATERAL MIXING
HEIGHT ABOVE GROUND
MIXING LAYER
TYPE 1
TYPE 2
HEIGHT ABOVE GROUND
TYPE 3
TYPE 4

Figure 4-11. Hypothesized models of the process that mixes tropopause folding events into the troposphere.

Source: Johnson and Viezee (1981)

by meteorological theory (Bjerknes, 1951) and by observations of surface ozone such as those made by Danielsen and Mohnen (1977), Lamb (1977), and Davis and Jensen (1976).

4.3.7 Stratospheric Ozone at Ground Level

After a detailed review of background tropospheric ozone, Viezee and Singh (1982) came to a number of important conclusions. First, as also concluded from earlier information, the stratosphere is a major but not the sole source of background ozone in the unpolluted troposphere. This stratospheric ozone is brought to the surface mixed layer by vertical mixing processes in the atmosphere that have been known for many years. In the northern hemisphere, between 30°N and 50°N, background surface ozone concentrations reach a maximum of 55 to 65 ppb. In the tropics, lower, 15 to 30 ppb, concentrations prevail. Viezee and Singh (1982) also noted that the stratospheric ozone reservoir has a strong seasonal variation, with a maximum in the spring and a minimum in fall and winter months, especially at middle latitudes. This seasonal cycle is reflected at ground-level background observation stations, where the average spring background ozone is generally in the range of 50 to 80 ppb and the average fall value is between 20 and 40 ppb. In the troposphere, concentrations generally increase gradually to the tropopause, but the seasonal pattern is the same.

Viezee and Singh (1982) concluded that relatively high ozone concentrations can occur for short periods of time, minutes to a few hours, over local areas as a result of stratospheric intrusions. They were able to document from published literature ten situations of probable intrusion of stratospheric ozone. These instances are shown in Table 4-1, reproduced from Viezee and Singh (1982). Note that all of the short-term situations in which peak concentrations exceeded 80 ppb occurred in winter and spring months and not in the photochemically active summer season. Of the three summer instances that were reported, two at Whiteface Mountain, New York, and one at Pierre, South Dakota, the highest reported concentration was 56 ppb for a 1-hr average.

A number of of stratospheric O_3 intrusions into the troposphere in Great Britain have been reported by Derwent et al. (1978). The results are noted as Case 4 in Table 4-1. The British measurements, made at Harwell, produced results similar to the United States TF data, indicating a general tropospheric O_3 background of 20 to 50 ppb based on hourly average concentrations, with

TABLE 4-1. DOCUMENTED EPISODES OF TRANSPORT OF STRATOSPHERIC OZONE TO GROUND LEVEL

Case no.	Date	Geographic location	Ground-level O_3 concentration, ppb	Duration of observed event	Length of data record examined	Source
1	3 March 1964	Quincy, Florida (near Tallahassee)	100 to 300	3 hr	July 1963 through July 1973	Davis and Jensen (1976)
2	26 February 1971	Observatory Hohenpeissenberg (1000 m MSL), SW of Munich, Germany	415 250	10 min 50 min	December 1970 through March 1971	Atmannspacher and Hartmannsgruber (1973)
3	19 November 1972	Santa Rosa, California	200 to 230	1 hr	November 1972	Lamb (1977)
4	6 March 1974	Harwell, Oxfordshire, England	110 to 115	2 hr	4 to 5 yr discontinuous	Derwent et al. (1978)
5	8,9 January 1975	Zugspitze Mountain, near Garmisch-Partenkirchen, Germany (3000 m MSL)	160 to 193	4 hr	August 1973 through February 1976	Singh et al. (1980)
9	11, 12 July 1975	Whiteface Mountain, New York (1150 m MSL)	$\leq$ 37	24-hr average	July 1975	Husain et al. (1977)
4	19 March 1977	Sibton, Suffolk, England	100 to 110	2 hr	4 to 5 yr discontinuous	Derwent et al. (1978)
10	24, 25, 28 June and 1 July 1977	Whiteface Mountain, New York	$\leq$ 47	24-hr average	June and July 1977	Dutkiewicz and Husain (1979)
6	4 March 1978	Denver, Colorado	82	1 hr	1975 to 1978	Haagenson et al. (1981)
7	July 1978	Pierre, South Dakota	$\leq$ 56 $\leq$ 46	1 hr 24-hr average	July through September 1978	Kelly et al. (1981)
8	15 March 1978	Kisatchie National Forest, Louisiana	100 to 105	2 hr	Spring 1978	Viezee et al. (1982)

Source: Viezee and Singh, 1982.

occasional short-period peaks of 100 ppb or so. Derwent et al. (1978) also made the statement, "These sporadic episodes appear to be observable only in rural areas and make no contribution to the exposure levels in urban areas" (Derwent et al., 1978). This comment, however, is contrary to the conclusions drawn by a number of investigators in the United States about the impact of ozone from natural sources, including TF events or general stratospheric injection, on ozone concentrations in urban areas. Some of the researchers who have come to such a conclusion include Coffey and Stasiuk (1975a), Coffey and Westberg (1977), and Coffey et al. (1977). On the other hand, Prior et al. (1981), using 9 a.m. ozone concentrations in St. Louis as input for a daily maximum ozone forecasting scheme, concluded that the concentrations they found in the morning may have represented transported rather than local ozone.

The downward transfer of air parcels and ozone from the stratosphere into the troposphere has been described above. There is, of course, a compensating transfer of tropospheric air upward into the lower stratosphere. Reiter (1975) has examined various mechanisms that contribute to this transfer. Air parcels moving out of the troposphere will carry with them the background concentrations of ozone that they had in the troposphere, and, as the air parcels mix in the stratosphere, these ozone molecules will become part of the stratospheric background ozone. Since the ozone concentrations are very much lower in the troposphere compared to the stratosphere, however, this exchange of tropospheric and stratospheric air parcels will not result in a net upward transport of ozone.

4.4 SUMMARY

The photochemistry of the polluted atmosphere is exceedingly complex, but an understanding of the basic phenomena is not difficult to acquire. Three processes occur: the emission of precursors to ozone, from (predominantly) manmade sources; photochemical reactions that take place during the dispersion and transport of these precursors; and scavenging processes that reduce the concentrations of both O_3 and precursors along the trajectory. Because transport and dispersion of the precursors determine the ambient concentrations ozone may finally reach, an understanding of certain meteorological phenomena, in addition to photochemical reactions, is also necessary. These latter are discussed first, followed by a presentation of important meteorological factors.

In the troposphere, O_3 is formed indirectly through the action of sunlight on nitrogen dioxide (NO_2). In the absence of competing reactions, a steady-state or equilibrium concentration of O_3 is soon established between the O_3, NO_2, and NO (nitric oxide). The injection of organic compounds (hydrocarbons) into the atmosphere upsets the equilibrium and allows the ozone to accumulate at much higher than steady-state concentrations. Recent work on the photochemistry of smog has demonstrated fairly conclusively that the hydroxyl radical, HO·, is the key species in causing organic compounds to play a major role in smog reactions.

The length of the induction period before the accumulation of O_3 begins depends heavily on the initial concentration of HO radicals. There is evidence that nitrous acid (HONO), which is a good source of HO radicals, occurs in the atmosphere, but at very low concentrations. The most important source of HO·, however, appears to be aldehydes, which are constituents of automobile exhaust, as well as decomposition products of most atmospheric photochemical reactions involving hydrocarbons.

The occurrence of organic compounds and sunlight does not mean that the photochemical reactions will continue indefinitely. Terminating reactions gradually remove NO_2 from the reaction mixtures, such that the photochemical cycles would slowly come to an end unless fresh NO and NO_2 emissions were injected into the atmosphere. Besides ozone, other oxidants that contain nitrogen, such as peroxyacetyl nitrate (PAN), nitric acid (HNO_3), and peroxynitric acid (HNO_4), as well as organic nitrates and inorganic nitrates, are some of the terminating compounds.

The maximum concentration that O_3 can reach in polluted atmospheres appears to depend on the hydrocarbon-nitrogen oxides ratio. At a low ratio (1:1 to 2:1), insufficient HO· radicals are available from the hydrocarbon species to effect the conversion of NO to NO_2, a necessary first step. At high ratios (greater than 12:1 to 15:1), conversion of NO to NO_2 occurs rapidly, but the terminating reactions remove NO_2 from the reaction cycles and O_3 cannot build up to high concentrations. Only at intermediate ratios (4:1 to 10:1) are conditions favorable to the formation of appreciable concentrations of O_3.

Recent studies on the fundamental photochemistry of organic compounds have been reasonably successful. The reactions of paraffinic compounds are fairly well understood, as are those of olefinic compounds. Photochemical reactions of the aromatic compounds, however, are poorly understood.

Natural hydrocarbons (i.e., those organic compounds emitted from vegetation) as well as hydrocarbons from manmade sources can react photochemically with nitrogen oxides to yield O_3, although natural hydrocarbons seem to be mainly scavengers of O_3 rather than producers of O_3.

Besides direct adverse effects on human health and on vegetation, O_3 contributes to visibility degradation and to acidic deposition. Through its photolysis by sunlight, with subsequent generation of HO radicals, ozone participates only indirectly, but not insignificantly, in the formation of both sulfate and nitrate aerosols, which cause reduced visibility. These sulfate and nitrate species, on further reaction, result in acidic precipitation.

Meteorological processes are quite important in determining the extent to which O_3 precursors can accumulate, and thereby the concentration of O_3 which can result. Atmospheric mixing depends principally on the amount of turbulent mixing, wind speed and direction, or both. Geography can have a significant impact, also, particularly at land-sea interfaces.

The degree of turbulent mixing can be characterized by atmospheric stability. Pollutants do not spread rapidly in stable layers, nor do they mix upwards rapidly through stable layers to higher altitudes. Rather, stable layers are usually characterized by temperature inversions, in which temperature increases with increasing altitude. Since pollutants emitted below or into an inversion layer will not readily mix across the inversion layer, they may persist for a considerable time and distance until the inversion is broken, usually by surface heating resulting from sunlight.

The extent to which surface heating can cause mixing heights to increase (and to cause dilution of O_3 and its precursors) is highly dependent on geography. Along both the Pacific Coast and the Northeast Coast, as well as near the Great Lakes, low-level inversions (i.e., the mixing height is not great) frequently persist through the afternoon, making these areas prone to local and regional air pollution episodes.

Wind speed and direction determine the extent to which pollutants can be increased by passing over successive sources, or can be diluted by being rapidly removed from the source area. The plumes of precursors and resulting O_3 from large metropolitan areas have been shown to persist for hundreds of miles. Three kinds of transport of ozone and other pollutants have been described, in terms of transport distance. In urban-scale transport, maximum concentrations of O_3 are produced about 20 miles or so (and about 2 to 3 hours) downwind from the major pollutant source areas. In mesoscale transport, O_3 has been observed up to 200 miles downwind from the sources of its precursors. Synoptic-scale transport is associated with large-scale, high-pressure air masses that may extend over and persist for many hundreds of miles.

The significance of sunlight in photochemistry is related to its intensity and its spectral distribution, both of which have direct effects on the specific chemical reaction steps that initiate and sustain oxidant formation. Days on which significant ozone-oxidant concentrations occur are usually days with warm, above-normal temperatures. These are also characteristic of high pressure systems with inversions and low winds. The photolysis of aldehydes is affected by the spectral distribution of light, since it is strongly dependent on wavelength in the near ultraviolet region.

Ozone formed in the stratosphere can be brought downwards to the earth's surface by events called "tropopause folds." These events are most commonly observed in the mid-latitudes during spring and early summer. Relatively high concentrations of O_3 can occur for short periods of time, minutes to a few hours, over local areas.

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5. PROPERTIES, CHEMISTRY, AND MEASUREMENT OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

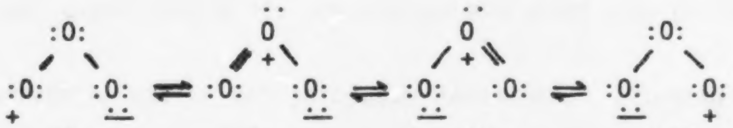
5.1 INTRODUCTION

The previous chapter presented information on the atmospheric chemistry of those compounds that serve as precursors to ozone and related photochemical oxidants in ambient air. That chapter included a discussion of the atmospheric processes that result in ozone and oxidant formation and also described the transport of those oxidants once formed. The present chapter deals with the physical and chemical properties and typical reactions ("type" reactions) of ozone and other oxidants, especially those properties and type reactions in ambient air and in solution-phase systems that are pertinent to understanding the direct effects of ozone and related photochemical oxidants on biological and nonbiological receptors. In addition, it presents detailed information on methods for measuring ozone and the two other most abundant photochemical oxidants (other than nitrogen dioxide) in ambient air, hydrogen peroxide and peroxyacetyl nitrate (PAN), along with its higher homologues. The information presented should prove to be an aid to state and local air pollution control agencies and to researchers investigating health and welfare effects. The chief reasons for presenting such information, however, are to provide relevant information (1) for understanding the general basis of the effects of ozone and other oxidants in biological systems; (2) for assessing the accuracy of aerometric data on these pollutants; and (3) for determining the impact of measurement and calibration biases on existing data on the health and welfare effects of ozone, total oxidants, and individual other oxidants.

5.2 PROPERTIES OF OZONE, PEROXYACETYL NITRATE, AND HYDROGEN PEROXIDE

5.2.1 Ozone

Ozone (O_3) is a triangularly shaped molecule consisting of three oxygen atoms arranged in four basic resonance structures:



(I) (II) (III) (IV)

The first and fourth structures, which predominate, are characterized by the presence of a terminal oxygen atom having only six electrons. The resonance forms depicted above have no unshared electrons. Thus, unlike other common oxidants in ambient air--oxygen (O_2) and nitrogen dioxide (NO_2)--ozone is not paramagnetic. Paramagnetism would impart free-radical properties to ozone. Ozone, then, does not itself behave as a free radical, though it is thought to give rise to free radicals in some biological and other aqueous systems (chapters 7, 9, and 10).

As the result of the presence of only six electrons on one of the oxygen atoms in ozone, the chemical reactions of ozone are electrophilic; that is, ozone removes electrons from or shares electrons with other molecules or ions. The terms "oxidant" and "oxidizing agent" characterize an ion, atom, or molecule that is capable of removing one or more electrons from another ion, atom, or molecule, a process called "oxidation." A "reducing agent" adds one or more electrons to another ion, atom, or molecule, a process called "reduction." Oxidation and reduction reactions occur in pairs and the coupled reactions are known as "redox reactions." In redox reactions, the oxidizing agent is reduced and the reducing agent is oxidized. The two components of such redox reactions are known as "redox pairs." The significance of redox reactions involving ozone is discussed in chapters 7 and 10. The capability of a chemical species for oxidizing or reducing is termed "redox potential" (positive or negative standard potential) and is expressed in volts. Ozone is a powerful oxidizing agent having a standard potential of +2.07 volts in aqueous systems (Weast, 1977).

Physical properties of ozone are given in Table 5-1 (U.S. Department of Health, Education, and Welfare, 1970, modified).

5.2.2 Peroxyacetyl Nitrate

Peroxyacetyl nitrate (PAN) has been observed as a constituent of photochemical smog in many localities, though its concentrations and its ratio to ozone differ from place to place (chapter 6). Peroxyacetyl nitrate, which has the formula $CH_3COO_2NO_2$, can exist in equilibrium with its decomposition products, NO_2 and acetylperoxy radicals, for long periods of time in the presence of sunlight, depending upon both temperature and the NO_2/NO ratio (Cox and Roffey, 1977).

The chief property of interest regarding PAN is its oxidizing ability. While no standard potential is available in the literature, PAN is known to be a more potent phytotoxicant, on a concentration basis, than ozone (chapter 7).

TABLE 5-1. PHYSICAL PROPERTIES OF OZONE

Physical state	Colorless gas
Chemical formula	O_3
Molecular weight	48.0
Melting point	-192.7 ± 0.2°C
Boiling point	-111.9 ± 0.3°C
Specific gravity relative to air	1.658
Vapor density	
At 0°C, 760 mm Hg	2.14 g/liter
At 25°C, 760 mm Hg	1.96 g/liter
Solubility at 0°C (Indicated volume of ozone at 0°C, 760 mm Hg)	0.494 ml/100 ml water
Henry's Law constant, 37°C and pH = 7	8666 atm/mole fraction[a]
Conversion factors	
At 0°C, 760 mm Hg	1 ppm = 2141 $\mu g/m^3$ 1 $\mu g/m^3$ = 4.670 x 10^{-4}
At 25°C, 760 mm Hg	1 ppm = 1962 $\mu g/m^3$ 1 $\mu g/m^3$ = 5.097 x 10^{-4} ppm

[a] Calculated by formula of Roth and Sullivan (1981).

Source: U.S. Department of Health, Education, and Welfare (1970), modified.

No evidence exists, however, to suggest that it is a comparably potent toxicant in animals or man (chapters 10 and 11).

A second property of PAN of interest it its thermal instability. In the laboratory, this thermal instability necessitates that precautions by taken in synthesizing, handling, and storing PAN, since improper handling and storage have resulted in explosions. The ready thermal decomposition of PAN results in a notable temperature dependence of PAN in ambient air (chapter 4).

Partly because of the thermal instability of PAN, its properties have not been as well characterized as those of O_3 or H_2O_2. Recent work on the physical properties of PAN, however, has confirmed data reported earlier, and results of the earlier and more recent work are shown in Tables 5-2 and 5-3 (Stephens,

TABLE 5-2. PHYSICAL PROPERTIES OF PEROXYACETYL NITRATE

Physical state, @25°C	Colorless liquid
Chemical formula	$CH_3COO_2NO_2$
Molecular weight	121
Boiling point, °C	106 ± 2^{a} 103.9^{b}
Triple point, °C	-50 ± 0.5^{a} -48 ± 0.5^{b}
Vapor pressure, @room temperature	~15 mm Hg
Vapor pressure curve	$\ln p = -4587/T + 18.76^{a,\,c}$ $\ln p = -4585/T + 18.79^{b}$
Hydrolysis	
In alkaline solution	Rate not available; products include nitrite ion and molecular oxygen[d]
In acidic solution @22°C, pH 5.6	$4 \times 10^{-4}\ \mathrm{sec}^{-1}$[e]
@25°C, pH 5.6	$6.8 \times 10^{-4}\ \mathrm{sec}^{-1}$[f]
Henry's Law constant, @10°C	$5 \pm 1\ \mathrm{M\ atm}^{-1}$[f]
Conversion factors	
@0°C, 760 mm Hg	1 ppm = 5398 μg/m³; 1 μg/m³ = 1.852×10^{-4} ppm
@25°C, 760 mm Hg	1 ppm = 4945 μg/m³; 1 μg/m³ = 2.022×10^{-4} ppm

Sources:

[a] Bruckmann and Wilner (1983).

[b] Kacmarek et al. (1978).

[c] Temperature, T, in °K; pressure, p, in torr.

[d] Stephens (1967); Nicksic et al. (1967).

[e] Lee et al. (1983).

[f] Holdren et al. (1984).

Source of remainder of data: U.S. Department of Health, Education, and Welfare (1970).

TABLE 5-3. INFRARED ABSORPTIVITIES OF PEROXYACETYL NITRATE AT APPROXIMATE RESOLUTION OF 1.2 cm^{-1} (RELATED TO 295°K AND 973 mb[a]) ($ppm^{-1}m^{-1} \times 10^4$)

	Frequency, cm^{-1}				
Reference	1842	1741	1302	1162.5	791.5
Bruckmann and Willner, 1983[b]	12.4	32.6	13.6	15.8	13.4
Stephens, 1969[c,d]	10.0	23.6	11.2	14.3	10.1

[a] Stephens (1979), personal communication, cited in Bruckmann and Willner (1983).

[b] Pure PAN.

[c] PAN in air.

[d] Stephens (1969).

1969; Bruckmann and Willner, 1983; Holdren et al., 1984; Kacmarek et al., 1978; U.S. Health, Education, and Welfare, 1970).

The infrared (IR) spectrum of PAN is important since most researchers rely on it for establishing concentrations of PAN for calibration. Bruckmann and Willner (1983) reported the IR spectrum of pure PAN and the Raman spectrum of liquid PAN at -40°C in an argon matrix (using an Ar^+ ion laser as the light source). The IR and Raman spectra found in their work are shown in Figure 5-1.

The recent work by Bruckmann and Willner (1983) also confirmed effects that correlate with the ultraviolet (UV) spectrum published earlier by Stephens (1969); that is, PAN was shown to be stable at $\lambda>300$ nm but was efficiently photolyzed at $\lambda<300$ nm (Bruckmann and Willner, 1983). Wavelengths pertinent to tropospheric pollutants are greater than 300 nm.

Though PAN is a strong phytotoxicant, it is important to mention here that PAN does not respond, or responds only negligibly, in measurements made by the Mast meter (section 5.5). It is a positive interference in ozone measurements made by the NBKI method (section 5.5). Since many of the early field studies on the effects of oxidants on vegetation utilized Mast meter measurements, this property of PAN relative to measurement methods is important.

5.2.3 Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is an oxidant that occurs in ambient air as part of the photochemical smog complex. It is thought to be formed through the

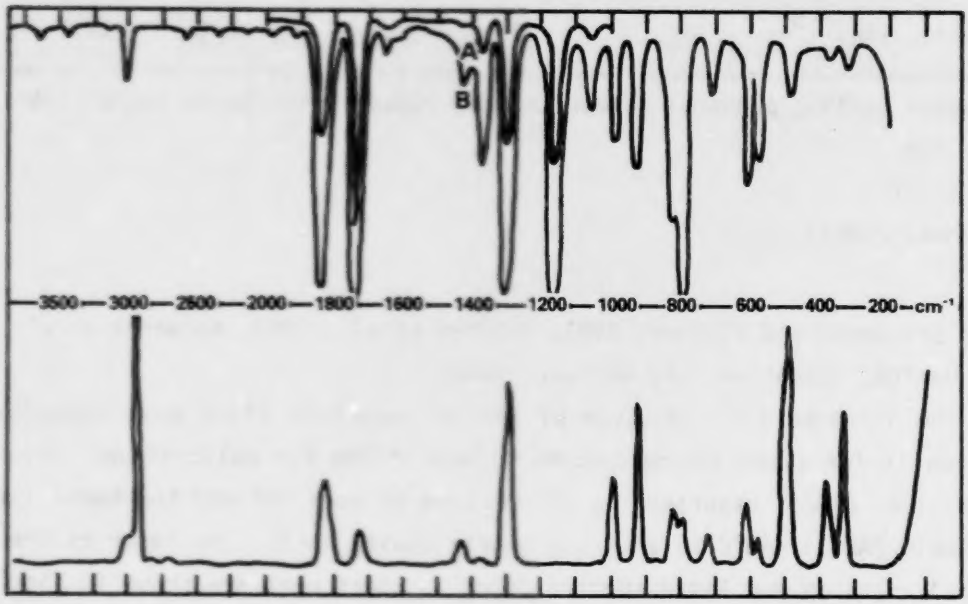


Figure 5-1. Top: IR gas spectrum of pure PAN (optical path length 10 cm); (A) 1.5 torr, (B) 10.0 torr. Bottom: Raman spectrum of PAN at -40°C (liquid); excitation light, 514.5 nm (100 mW).

Source: Bruckmann and Willner (1983).

recombination of two hydroperoxy radicals ($HO_2\cdot$) in the presence of a third, energy-absorbing molecule (chapter 4; section 5.5.8).

In aqueous media, H_2O_2 is an inorganic acid that has a dissociation constant of 2.4×10^{-12} and a pK of 11.62 (at 25°C) (Weast, 1977). In the redox pair H_2O_2/H_2O, hydrogen peroxide has a standard potential of ±1.776 volts (Weast, 1977), compared with the comparable standard potential for ozone of +2.07 volts.

Pertinent physical properties of H_2O_2 are given in Table 5-4 (Weast, 1977).

TABLE 5-4. PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE

Physical state, @25°C	Colorless liquid
Chemical formula	H_2O_2
Molecular weight	34.01
Melting point, °C	-0.41
Boiling point, °C, @760 mm Hg	150.2
Density, @25°C, 760 mm Hg	1.4422
Vapor pressure, @16.3°C	~1 mm Hg
Conversion factors	
@0°C, 760 mm Hg	1 ppm = 1520 $\mu g/m^3$; 1 $\mu g/m^3$ = 6.594×10^{-4} ppm
@25°C, 760 mm Hg	1 ppm = 1390 $\mu g/m^3$; 1 $\mu g/m^3$ = 7.195×10^{-4} ppm

Source: Weast (1977).

Additional properties should be noted here that are of interest relative to whether effects of H_2O_2 in biological receptors are of significance. First, H_2O_2, though classed as a reasonably strong oxidant on the basis of its standard potential for the redox system H_2O_2/H_2O, has been reported to be a positive interference in measurements of total oxidants made by the Mast meter but to give a very slow response (slow color development) in the NBKI method for total oxidants (section 5.5). This difference should be borne in mind when effects attributed to oxidants, as opposed to ozone, are evaluated.

Second, H_2O_2 occurs normally as a substrate in biological systems and is involved in several redox pairs of biological importance, as shown in Table 5-5. It should also be noted that enzymes are present, at least in mammalian systems, that catalyze the breakdown of H_2O_2.

TABLE 5-5. NORMAL ELECTRODE POTENTIALS OF SOME HYDROGEN PEROXIDE-CONTAINING OXIDATION-REDUCTION SYSTEMS OF BIOLOGICAL IMPORTANCE

System	Potential (E'_0), volts
HO_2/H_2O_2	+1.12
$H_2O_2/HO^{\cdot} + H_2O$	+0.38
$\frac{1}{2}O_2/H_2O_2$	+0.30

Source: West et al. (1966).

5.3 ATMOSPHERIC REACTIONS OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

5.3.1 Introduction

The atmospheric reactions of ozone and other photochemical oxidants such as peroxyacetyl nitrate (PAN) and hydrogen peroxide (H_2O_2) are complex and diverse. The reactions of these species result in products and processes that may have significant environmental implications, including effects on biological systems, nonbiological materials, and such phenomena as visibility degradation and acidification of cloud and rain water.

Ozone, for example, is highly reactive toward certain classes of organic compounds (e.g., alkenes) and certain reactions of ozone with alkenes lead to the formation of secondary organic aerosols. Photolysis of ozone leads to the formation of $O(^1D)$ atoms and, by subsequent reactions, the production of OH radicals. Ozone may also play a role in the oxidation of SO_2 to H_2SO_4, both indirectly in the gas phase (via formation of OH radicals and Criegee biradicals) and directly in aqueous droplets. Evidence is also accumulating that hydrogen peroxide, like ozone, is involved in both gas-phase photochemistry and aqueous-phase oxidations. For example, studies of the rates of oxidation of SO_2 by H_2O_2 in solution suggest that this reaction is sufficiently fast that it could be the major aqueous-phase oxidation route for SO_2, under at least some atmospheric conditions. In addition, the importance of oxidants such as PAN to various aspects of atmospheric chemistry, such as long-range transport of NO_x and multi-day air pollution episodes, is now being recognized.

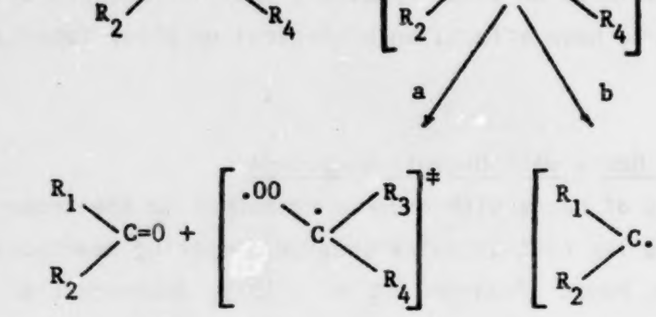
In the following sections, the present state of knowledge concerning the atmospheric reactions of O_3, PAN, H_2O_2, and formic acid (HCOOH) are summarized in some detail, including the mechanisms of certain of these reactions. Emphasis is placed, whenever possible, on those reactions that lead to products or processes suspected or known to have effects on biological or other important receptors.

5.3.2 Atmospheric Reactions of Ozone with Organic Compounds

In discussing the reactions of ozone with organic compounds in the troposphere, it is important to recognize that organics undergo competing reactions with OH radicals during daytime hours (Atkinson et al., 1979; Atkinson and Lloyd, 1984) and, in certain cases, with NO_3 radicals during nighttime hours (Japar and Niki, 1975; Carter et al., 1981a; Atkinson et al., 1984a,b,c,d), as well as photolysis. Thus, all organics except the perhaloalkanes exhibit room-temperature OH radical rate constants of $\gtrsim 5 \times 10^{-15}$ cm^3 $molecule^{-1}$ sec^{-1} (Atkinson et al., 1979; Jeong and Kaufman, 1982). Since the ratio of O_3 to OH radical concentrations in the unpolluted troposphere during daylight hours is believed to be of the order of 10^6 (Singh et al., 1978; Crutzen, 1982), only for these organics whose O_3 reaction rate constants are greater than $\sim 10^{-21}$ cm^3 $molecule^{-1}$ sec^{-1} can consumption by O_3 be considered to be atmospherically important (Atkinson and Carter, 1984). Although these ozone reactions of interest are summarized below, the recent reviews by Atkinson and Carter (1984) and Atkinson and Lloyd (1984) should be consulted for a detailed and comprehensive discussion of the kinetics and mechanisms of the atmospheric reactions of ozone with organic compounds.

5.3.2.1 Alkenes. Ozone reacts rapidly with the acyclic mono-, di-, and trialkenes and with cyclic alkenes. The rate constants for these reactions range from $\sim 10^{-18}$ to $\sim 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1} (Atkinson and Carter, 1984), corresponding to atmospheric lifetimes ranging from a few minutes for the more reactive cyclic alkenes, such as the monoterpenes, to several days. In polluted atmospheres, especially in the afternoons during photochemical oxidant episodes, a significant portion of the consumption of the more reactive alkenes will occur via reaction with O_3, rather than with OH radicals.

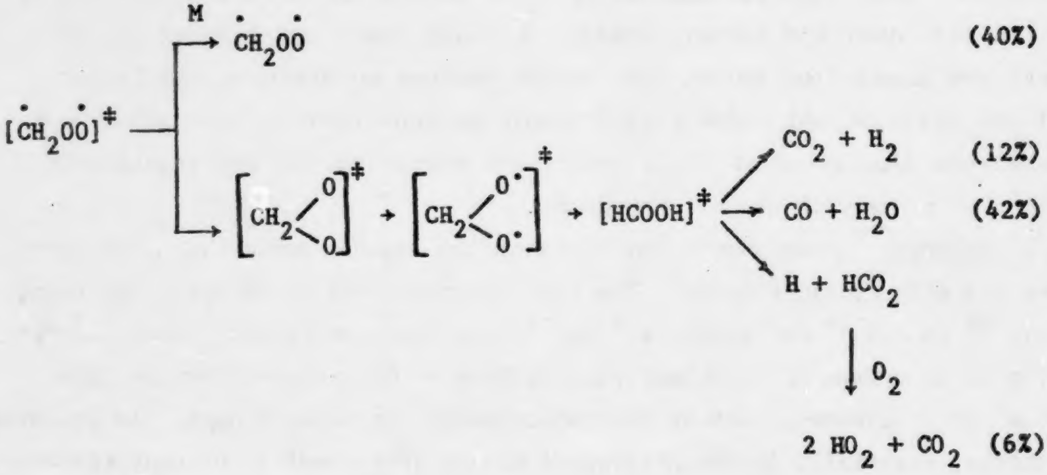
It is now reasonably well-established that the initial step in the ozone-alkene reaction involves the formation of a "molozonide," which rapidly decomposes (Harding and Goddard, 1978; Herron et al., 1982) to a carbonyl compound and a biradical (which is also initially energy-rich):


O_3 +
R_1
R_2
C=C
R_1
R_4
O
O
O
R_1
R_2
C
C
R_3
R_4
‡
a
b
R_1
R_2
C=O +
.OO
C
R_3
R_4
‡
R_1
R_2
C.
O-O·
‡
+ O=C
R_3
R_4

(5-1)

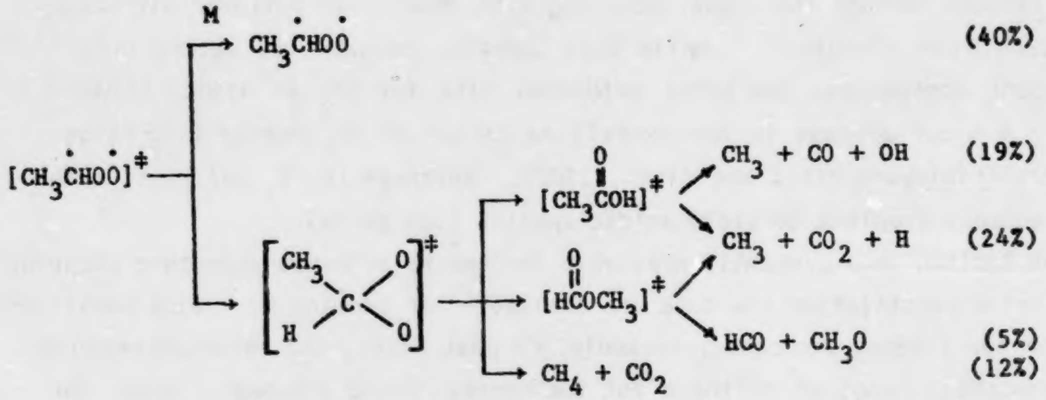
where $[\ ]^{\ddagger}$ denotes an energy-rich species.

Based on analyses of reported product and mechanistic studies of the reactions of O_3 with ethene and propene and the much less extensive studies of the higher alkenes, Atkinson and Lloyd (1984) have suggested that these initially energy-rich biradicals react under atmospheric conditions as shown below:


M
$\dot{C}H_2O\dot{O}$
(40%)
$[\dot{C}H_2O\dot{O}]^{\ddagger}$
$[CH_2<^{O}_{O}]^{\ddagger}$
$[CH_2<^{O\cdot}_{O\cdot}]^{\ddagger}$
$[HCOOH]^{\ddagger}$
$CO_2 + H_2$
(12%)
$CO + H_2O$
(42%)
$H + HCO_2$
O_2
$2\ HO_2 + CO_2$
(6%)

(5-2)

and


M
$CH_3\dot{C}HO\dot{O}$
(40%)
$[CH_3\dot{C}HO\dot{O}]^{\ddagger}$
$[CH_3\overset{O}{\overset{\|}{C}}OH]^{\ddagger}$
$CH_3 + CO + OH$
(19%)
$CH_3 + CO_2 + H$
(24%)
$[HCOCH_3]^{\ddagger}$
$HCO + CH_3O$
(5%)
$CH_4 + CO_2$
(12%)

(5-3)

where $\dot{C}H_2\dot{O}O$ and $CH_3\dot{C}HO\dot{O}$ denote thermalized biradicals. These thermalized biradicals have been shown (Calvert et al., 1978; Herron et al., 1982; Atkinson and Carter, 1984) to undergo bimolecular reactions with aldehydes, SO_2, CO, and H_2O; and it is believed that they will also react with NO and NO_2.

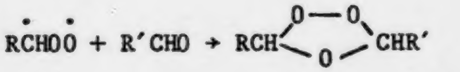
$$R\dot{C}HO\dot{O} + NO \rightarrow RCHO + NO_2 \qquad (5\text{-}4)$$

$$R\dot{C}HO\dot{O} + NO_2 \rightarrow RCHO + NO_3 \qquad (5\text{-}5)$$

$$R\dot{C}HO\dot{O} + SO_2 \xrightarrow{H_2O} RCHO + H_2SO_4 \qquad (5\text{-}6)$$

$$R\dot{C}HO\dot{O} + H_2O \rightarrow RCOOH + H_2O \qquad (5\text{-}7)$$

$$R\dot{C}HO\dot{O} + CO \rightarrow \text{products} \qquad (5\text{-}8)$$

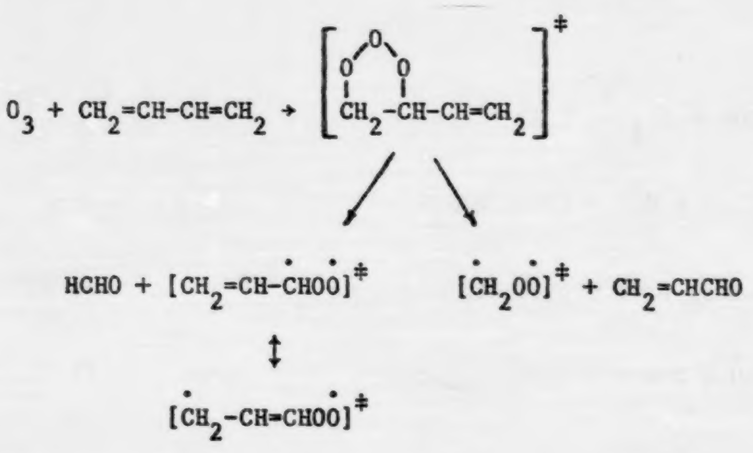

$R\dot{C}HO\dot{O} + R'CHO \rightarrow RCH$
O—O
O
CHR'

(5-9)

Under atmospheric conditions, the reactions with NO, NO_2, or H_2O are expected to be the dominant loss processes of these thermalized biradicals, with the precise major reaction pathway depending on the relative concentrations. Hence, in the atmosphere, ozone-alkene reactions can lead ultimately to the formation of aldehydes and acids, as well as to the conversion of SO_2 to H_2SO_4. Unlike the case for other free radicals, oxidation of SO_2 by these biradicals can take place at night, since ozone can remain aloft at significant concentrations through the night, reacting with alkenes in polluted air masses to produce such biradicals. While this appears, however, to be the only significant homogeneous gas-phase oxidation rate for SO_2 at night, it is probably a minor process in the overall oxidation of SO_2 during long-range transport (Finlayson-Pitts and Pitts, 1982). Furthermore, O_3 can react with SO_2 in aqueous droplets to yield acidic species (see below).

The limited data presently available for the haloalkenes show that fluorine and chlorine substitution (no data are available for bromine or iodine substituents) on the alkenes decreases, markedly, in most cases, the room-temperature rate constants, compared to those for the corresponding alkenes. Hence, for the haloalkenes studied to date (Atkinson and Carter, 1984), their reactions with ozone are of minor importance under atmospheric conditions, compared to reactions with OH radicals.

While the above mechanistic discussion applies mainly to the simple acyclic monoalkenes, the initial reactions for the di- and poly-alkenes, the cyclic alkenes, and the haloalkenes are believed to be analogous (Niki et al., 1983; Zhang et al., 1983). For example, for 1,3-butadiene, cyclohexene, and vinyl chloride, the reactions are expected to proceed via:



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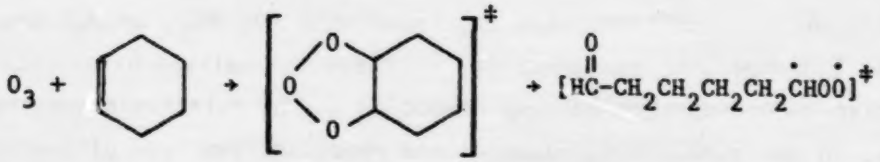

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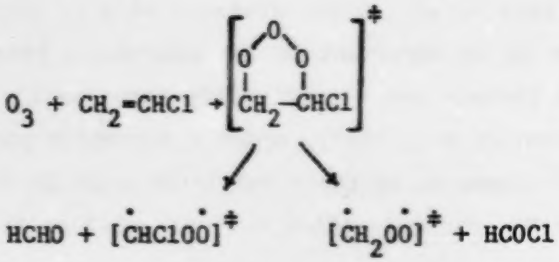
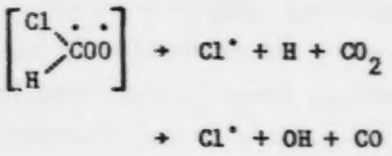


(5-13)

with the initially energy-rich biradicals undergoing subsequent reactions. The excited halogenated biradicals such as [CHClOȮ] are expected to decompose to form Cl atoms and other radical species (Niki et al., 1983):



(5-14)

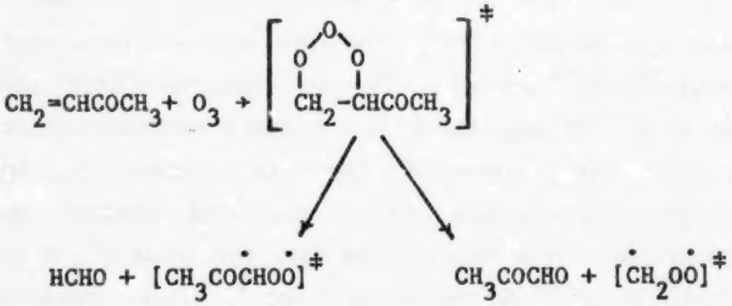
The modes of reaction under atmospheric conditions of the more complex excited biradicals, such as $[CH_2{=}CH{-}\dot{C}HO\dot{O}]$ and $[HCO(CH_2)_4\dot{C}HO\dot{O}]$ shown above, are, however, presently unknown.

5.3.2.2 Alkanes and Alkynes. At the present time, there appears to be no convincing evidence in the literature for an elementary reaction between O_3 and the alkanes (Atkinson and Carter, 1984). The reported rate constants of 10^{-23} to 10^{-26} cm^3 $molecule^{-1}$ sec^{-1} are thus clearly unimportant under atmospheric conditions. Similarly, although there is presently substantial uncertainty (Atkinson and Carter, 1984) concerning the rate constants for the reactions of ozone with the simple alkynes (e.g., acetylene, propyne, and 1-butyne), most of the available room temperature data for these $\leq C_4$ alkynes fall in the range of $\sim 10^{-20}$ to 10^{-19} cm^3 $molecule^{-1}$ sec^{-1}. Thus, those reactions will also be unimportant in the atmosphere, since the corresponding OH radical rate constants are, for example, $\sim 7 \times 10^{-13}$ and $\sim 7 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} for acetylene and propyne and 1-butyne, respectively (Atkinson and Aschmann, 1984).

5.3.2.3 Aromatics. As in the case of the alkanes, the aromatic hydrocarbons react only very slowly with O_3 (Pate et al., 1976; Atkinson et al., 1982) and these reactions are not expected to be important in the atmosphere (Atkinson and Carter, 1984). Although the cresols are significantly more reactive than the aromatic hydrocarbons (Atkinson et al., 1982), under atmospheric conditions their reactions with O_3 are minor compared to their reactions with OH radicals (Atkinson et al., 1978; 1982) or NO_3 radicals (Carter et al., 1981a; Atkinson et al., 1984d).

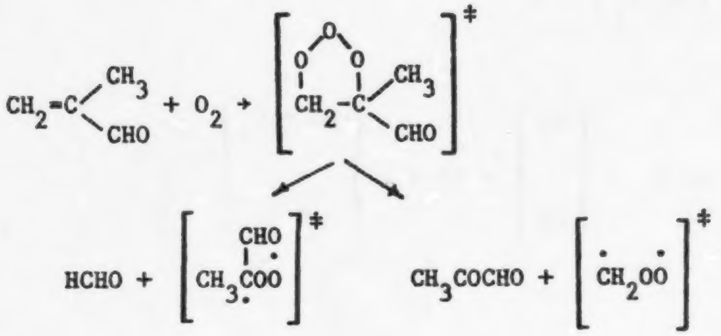
5.3.2.4 Oxygen-Containing Organics. For those oxygen-containing compounds that do not contain unsaturated carbon-carbon bonds (e.g., formaldehyde, acetaldehyde, glyoxal, and methylglyoxal), the reactions with ozone are very slow, and, by analogy, this is expected to be the case for all ethers, alcohols, aldehydes, and ketones not containing unsaturated carbon-carbon bonds. For the carbonyls and ethers (other than ketene) that contain unsaturated carbon-carbon bonds, however, much faster reactions are observed (Atkinson et al., 1981).

Few data are available, however, concerning the mechanisms of the reactions of O_3 with such oxygen-containing organics, the only published information being that of Kamens et al. (1982). From a study of the reactions of O_3 with methacrolein and methyl vinyl ketone, methylglyoxal was observed as a product, along with other minor products (Kamens et al., 1982), as anticipated from the reaction schemes.


CH_2=$CHCOCH_3$ + O_3 →
O
O O
CH_2-$CHCOCH_3$
‡
HCHO + [$CH_3\dot{C}OCHO\dot{O}$]‡
CH_3COCHO + [$\dot{C}H_2O\dot{O}$]‡

(5-15)

and



(5-16)

5.3.2.5 Nitrogen-Containing Organics. While the kinetics of the reactions of O_3 with a variety of nitrites, nitriles, nitramines, nitrosoamines, amines, and hydrazines have been studied (Atkinson and Carter, 1984), only for the hydrazines are these reactions sufficiently rapid to be of atmospheric importance. Indeed, hydrazine, monomethylhydrazine, and 1,1- (or unsymmetrical-) dimethylhydrazine react sufficiently rapidly with O_3 (with rate constants of $\sim 3 \times 10^{-17}$ cm^3 $molecule^{-1}$ sec^{-1} for hydrazine and $\geq 10^{-15}$ cm^3 $molecule^{-1}$ sec^{-1} for monomethylhydrazine, and 1,1-dimethylhydrazine [Tuazon et al., 1982] that their major atmospheric reactions are likely to be via reaction with O_3. The initial reactions are not completely understood, but for hydrazine, monomethylhydrazine, and 1,1-dimethylhydrazine, they appear to involve H-atom abstraction from the weak N-H bonds to form an OH radical.

$$R_1R_2NNH_2 + O_3 \rightarrow R_1R_2N\dot{N}H + OH + O_2 \qquad (5\text{-}17)$$

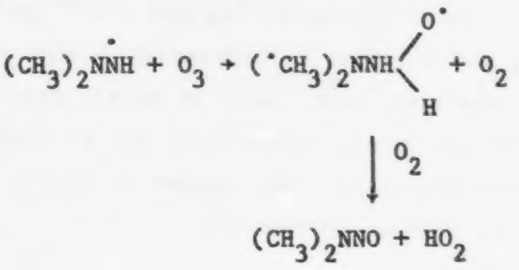
Using FT-IR absorption spectroscopy, Tuazon et al. (1981a, 1982) have obtained extensive product data concerning the reactions of N_2H_2, CH_3NHNH_2, and $(CH_3)NNH_2$ with O_3; and these data have allowed plausible reaction pathways to be postulated. In these reaction schemes, the $R_1R_2N\dot{N}H$ radicals [where R_1, R_2 = H or CH_3 for the hydrazines N_2H_4, CH_3NHNH_2, and $(CH_3)_2NNH_2$] are proposed to react as follows:

For $RNH\dot{N}H$ or $R\dot{N}NH_2$ radicals:

$$\left\{\begin{matrix}\mathrm{RNH\dot{N}H}\\ \\ \mathrm{R\dot{N}NH_2}\end{matrix}\right\} + O_2 \rightarrow \mathrm{RN{=}NH} + HO_2 \qquad (5\text{-}18)$$

$$\mathrm{RN{=}NH} + \left\{\begin{matrix}O_3\\ \\ OH\end{matrix}\right\} \rightarrow \begin{array}{c}\mathrm{RN{=}\dot{N}}\\ \big\downarrow\\ R + N_2\end{array} + \left\{\begin{matrix}OH + O_2\\ \\ H_2O\end{matrix}\right\} \qquad (5\text{-}19)$$

though additional (and more uncertain) reactions, giving rise to diazomethane and other products, occur for R=CH_3 (Tuazon et al., 1981a; Carter et al., 1981b). For the $(CH_3)_2N\dot{N}H$ radical, this reaction sequence cannot occur, and Tuazon et al. (1981a) have postulated other pathways leading to N-nitrosodimethylamine, the major observed product.



(5-20)

or

$$\begin{array}{c}(CH_3)_2N\dot{N}H + O_2 \rightarrow (CH_3)_2\overset{+}{N}{=}\overset{-}{N} + HO_2\\ \big\downarrow O_3\\ (CH_3)_2NNO + O_2\end{array} \qquad (5\text{-}21)$$

The N-nitrosodimethylamine observed in this system by FT-IR spectroscopy (Tuazon et al., 1981a) is considered to be a carcinogen (Andrews et al., 1978; Rao, 1979). Despite this progress, significant uncertainties and inconsistencies remain in the present understanding of these reactions of O_3 with these simple hydrazines (N_2H_4, CH_3NHNH_2, and $(CH_3)_2NNH_2$).

The sole information concerning the gas-phase reaction of O_3 with diazenes, diazomethane, and hydrazones is that of Tuazon et al. (1982). These species were observed to be products in the reactions of the simple hydrazines with O_3 (see above) or of hydrazine with formaldehyde; and were observed to react further when formed in the presence of O_3.

5.3.2.6 Sulfur-Containing Organics. Based upon the kinetic data available for dimethyl sulfide, thiirane, and thiophene, it appears at the present time that the rates of reaction of O_3 with sulfur-containing organics can be considered to be unimportant for atmospheric purposes (Atkinson and Carter, 1984).

5.3.2.7 Other Reactions

5.3.2.7.1 Organometallics. To date, rate constants have been reported only for tetramethyl- and tetraethyl-lead (Harrison and Laxen, 1978). No mechanistic or product data are available for these reactions; but it is possible that the reactions proceed via initial H-atom abstraction from the alkyl C-H bonds, e.g.:

$$Pb(CH_3)_4 + O_3 \rightarrow \overset{\bullet}{C}H_2Pb(CH_3)_3 + OH + O_2 \qquad (5\text{-}22)$$

$$Pb(C_2H_5)_4 + O_3 \rightarrow CH_3\overset{\bullet}{C}HPb(C_2H_5)_3 + OH + O_2 \qquad (5\text{-}23)$$

5.3.2.7.2 Radical species. Because of the low concentration of O_3 and radicals in the atmosphere, and because both alkyl and most alkoxy radicals react at significant rates with O_2 (which is present at a concentration $>10^5$ higher than O_3 in ambient atmospheres), these reactions can be considered to be of negligible importance in the atmosphere.

5.3.2.8 Atmospheric Lifetimes. Table 5-6 compares the room-temperature rate constants and the approximate corresponding atmospheric loss rate constants for reaction with O_3 (over a 24-hour period), with OH radicals during daytime hours, and with NO_3 radicals during nighttime hours.

It can be seen that under these atmospheric conditions the reactions with O_3 are important for the higher alkenes, including the monoterpenes, and for the hydrazines. For the other organics for which kinetic data are available, their reactions with O_3 are generally of negligible or minor importance.

5.3.2.9 Aerosol Formation. The reaction of ozone with alkenes having six or more carbon atoms and with cyclic alkenes and conjugated alkenes has been shown to lead to the formation of secondary organic aerosols (National Academy of Sciences, 1977; Scheutzle and Rasmussen, 1978). For ambient concentrations of ozone, the amount of aerosol formation is generally greater the higher the carbon number, and classes of organics such as the terpenes are very efficient at producing aerosol.

A spectrum of products have been identified as constituents of secondary organic aerosols. These include a wide range of carboxylic and dicarboxylic acids, aldehydes, alcohols, and other oxygenated compounds. The chemical pathways leading to these products are exceedingly complex and are far from well-characterized. Many of the studies, however, in which products have been

TABLE 5-6. CALCULATED LIFETIMES OF SELECTED ORGANICS RESULTING FROM ATMOSPHERIC LOSS BY REACTION WITH O_3 AND WITH OH AND NO_3 RADICALS

	Organic lifetimes,[a] τ		
Organic compound	O_3, 24-hour	OH, daytime	NO_3, nighttime
Anthropogenic alkenes			
Ethene	2.7 days	16 hr	79 days
Propene	11 hr	5.6 hr	1.1 days
trans-2-Butene	35 min	2.0 hr	33 min
2-Methyl-2-butene	17 min	1.6 hr	1.3 min
2,3-Dimethyl-2-butene	6 min	1.3 hr	0.2 min
Naturally emitted alkenes			
Isoprene	10 hr	1.4 hr	22 min
α-Pinene	1.4 hr	2.3 hr	2 min
β-Pinene	5.5 hr	1.8 hr	5 min
Δ^3-Carene	1.0 hr	1.7 hr	1.2 min
d-Limonene	11 min	1.0 hr	0.9 min
Hydrazines			
Hydrazine	~1.9 hr	1.4 hr	-
Monomethyl hydrazine	<4 min	1.4 hr	-

[a] Assuming 100 ppb of O_3 (24-hr average), 2×10^6 cm^{-3} (0.08 ppt) of OH during daylight hours, and 100 ppt of NO_3 during nighttime hours.

identified, were carried out at organic precursor concentrations greatly exceeding their ambient levels. Hence, it is still not totally clear whether organic-O_3 reactions under ambient-atmosphere conditions lead to significant amounts of aerosol formation.

Regardless of the chemistry involved, however, the condensation of such products into particles which then grow into the light-scattering size range (~0.1 to 1 μm) can contribute to visibility reduction in both urban airsheds and in natural environments.

5.3.3 Atmospheric Reactions of Ozone with Inorganic Compounds and with Light

Ozone reacts rapidly with NO to form NO_2:

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (5\text{-}24)$$

Because this reaction is rapid, ozone concentrations in urban atmospheres cannot rise significantly until most of the NO emitted from combustion sources has been converted to NO_2. Ozone can react with NO_2 to produce the nitrate (NO_3) radical and an oxygen molecule:

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \qquad (5\text{-}25)$$

The NO_3 radical has recently been shown to be an important sink for certain classes of organic compounds, including several of the monoterpenes and dimethyl sulfide (Winer et al., 1984).

Photolysis of ozone can be a significant pathway for formation of OH radicals, particularly during mid-afternoon when O_3 concentrations are at a maximum in urban airsheds:

$$O_3 + h\nu\ (\lambda < 319\ \text{nm}) \rightarrow O(^1D) + O_2(^1\Delta) \qquad (5\text{-}26)$$

$$O(^1D) + H_2O \rightarrow 2\ OH \qquad (5\text{-}27)$$

The reaction of the $O(^1D)$ atoms, formed from O_3 photolysis, with water vapor occurs with about 20 percent efficiency at ambient temperatures and about 50 percent relative humidity, with about 80 percent of the $O(^1D)$ atoms being quenched to $O(^3P)$ atoms by N_2 and O_2.

5.3.4 Reactions of Ozone in Aqueous Droplets

While the thermal oxidation of SO_2 by ozone in the gas phase appears to be too slow to be important in acid deposition phenomena, the role of ozone in oxidizing SO_2 dissolved in water droplets (e.g., cloud, fog, or rain) may be of considerable significance. At 25°C, ozone has a Henry's Law constant of 10^{-2} mol L^{-1} atm^{-1} (Kirk-Othmer, 1981). Given ambient concentrations ranging from 30 to about 300 ppb, O_3 would be expected to have concentrations in aqueous droplets in the atmosphere of approximately 3-30 x 10^{-10} mol L^{-1}. The rate of reaction between O_3 and SO_2, when both are dissolved in aqueous droplets, has been shown in laboratory studies to be relatively fast (Penkett et al., 1979; Kunen et al., 1983; Martin, 1984; Hoffman et al., 1984; Schwartz, 1984; Brock and Durham, 1984), although the rate of this reaction is pH-dependent and decreases as the acidity of the solution increases.

Figure 5-2 shows data reported by Schwartz (1984) for the rate of aqueous-phase oxidation of S(IV) by 30 ppb of O_3 (and also by 1 ppb of H_2O_2) as a function of solution pH. The aqueous-phase oxidation rate, R, per part-per-billion SO_2 partial pressure decreases with decreasing pH by roughly a factor of 20 per pH unit. This pH dependence reflects the solubility of S(IV) as well as a slight pH dependence of the second-order rate constant for the oxidation of S(IV) by O_3 (Erickson et al., 1977; Larson et al., 1978; Penkett et al., 1979). Schwartz (1984) concluded, from consideration of these data and uptake times for SO_2, that oxidation of SO_2 by O_3 cannot produce solution pH values below ~4.5. Schwartz (1984), however, has also interpreted the field data of Hegg and Hobbs (1981) for sulfate production rates at the inflow and outflow regions of lenticular clouds as being consistent with the aqueous-phase oxidations of S(IV) by O_3.

An additional aspect of the role of O_3 in the chemistry of aqueous droplets concerns its photolysis to yield OH radicals in solution (Graedel and Weschler, 1981; Chameides and Davis, 1982):

$$(O_3)_{aq} + h\nu \rightarrow (O(^1D))_{aq} + O_2\ (aq) \qquad (5\text{-}28)$$

$$O(^1D)_{aq} + (H_2O)_{aq} \rightarrow 2(OH)_{aq} \qquad (5\text{-}29)$$

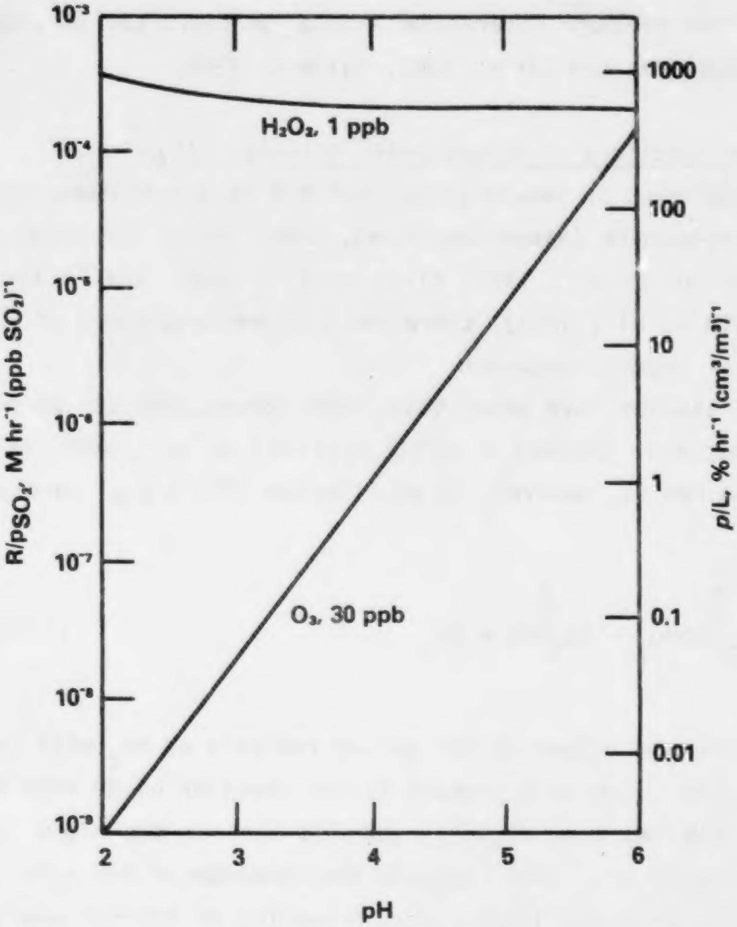


Figure 5-2. Rate of aqueous-phase oxidation of S(IV) by O_3 (30 ppb) and H_2O_2 (1 ppb), as a function of solution pH. Gas-aqueous equilibria are assumed for all reagents. R/p_{SO_2} represents aqueous reaction rate per ppb of gas-phase SO_2; p/L represents rate of reaction referred to gas-phase SO_2 partial pressure per cm^3—m^{-3} liquid water volume fraction (Schwartz, 1984).

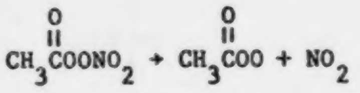
and its reactions with aqueous OH^- ions and H_2O_2 to yield aqueous HO_2 radicals (Chameides and Davis, 1982). The OH radicals formed by this in situ process can result in the oxidation of S(IV).

For discussions of possible mechanisms for the oxidation of SO_2 by O_3 in aqueous systems, the primary literature should be consulted (Graedel and Weschler, 1981; Chameides and Davis, 1982; Calvert, 1984).

5.3.5 Atmospheric Reactions of Peroxyacetyl Nitrate (PAN)

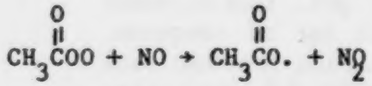
With the recognition in recent years that PAN is a ubiquitous nitrogenous species in the troposphere (Singh and Hanst, 1981; Singh and Salas, 1983a; Penkett, 1983; Spicer et al., 1983; Aikin et al., 1983) and in the lower stratosphere (Aikin et al., 1983), there has been renewed focus on the atmospheric role of this organic compound.

Smog-chamber studies have shown that, once formed, PAN can be relatively stable under atmospheric thermal conditions (Pitts et al., 1979; Akimoto et al., 1980). Since PAN is, however, in equilibrium with acetyl peroxy radicals and NO_2,

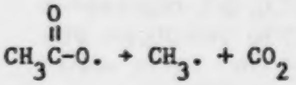


$$CH_3\overset{\overset{O}{\|}}{C}OONO_2 \rightarrow CH_3\overset{\overset{O}{\|}}{C}OO + NO_2 \qquad (5\text{-}30)$$

any process that removes either acetyl peroxy radicals or NO_2 will lead to the decomposition of PAN. One such process is the reaction of NO with $CH_3C(O)O_2$ radicals. Since PAN has been shown to persist through the night in urban atmospheres (Tuazon et al., 1980; 1981b), the reaction of PAN with NO during the morning traffic peak can lead to the formation of OH radicals via the following mechanism (Carter et al., 1981c):



$$CH_3\overset{\overset{O}{\|}}{C}OO + NO \rightarrow CH_3\overset{\overset{O}{\|}}{C}O. + NO_2 \qquad (5\text{-}31)$$



$$CH_3\overset{\overset{O}{\|}}{C}\text{-}O. \rightarrow CH_3. + CO_2 \qquad (5\text{-}32)$$

$$CH_3. + O_2 \xrightarrow{M} CH_3OO. \qquad (5\text{-}33)$$

$$CH_3OO. + NO \rightarrow CH_3O. + NO_2 \qquad (5\text{-}34)$$

$$CH_3O. + O_2 \rightarrow HO_2 + HCHO \qquad (5\text{-}35)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (5\text{-}36)$$

$$OH + NO \xrightarrow{M} HONO \qquad (5\text{-}37)$$

$$OH + NO_2 \xrightarrow{M} HNO_3 \qquad (5\text{-}38)$$

Thus, the reaction of PAN carried over from previous air pollution episodes with NO will lead to enhanced smog formation on subsequent days. This enhancement in reactivity results both from the fact that these reactions form radicals that initiate the transformations occurring in photochemical smog and from the fact that these reactions convert NO to NO_2, which allows earlier formation of O_3 and higher levels to be attained. It should be noted that this enhancement will result even if all of the PAN reacts with NO emitted at nighttime, since the NO conversion does not require sunlight; and at least some of the radicals formed will be "stored" as nitrous acid, to be released when photolysis begins at sunrise.

These results could have important implications regarding multiday photochemical pollution episodes in which significant buildup of PAN is observed. Under such conditions, carry-over of PAN may be a significant factor in promoting ozone formation on subsequent days and may, in part, contribute to the progressively higher O_3 levels often observed during such episodes (Tuazon et al., 1980; 1981b).

A second important role of PAN is its ability to contribute to the long-range transport of NO_x. In the absence of significant levels of NO (i.e., in the cleaner troposphere) and in regions of lower temperature and in the upper troposhere, when the thermal decomposition of PAN becomes unimportant, the atmospheric lifetime of PAN will be determined by its reaction with OH radicals. This reaction is sufficiently slow (Singh and Hanst, 1981) that PAN will probably be long-lived and serve, hence, as a reservoir for odd nitrogen in a manner analogous to HNO_3 (Aikin et al., 1983).

5.3.6 Atmospheric Reactions of Hydrogen Peroxide

Although hydrogen peroxide formed in the gas phase from the reactions of hydroperoxyl radicals plays a role in HO_x chemistry in the troposphere, and especially in the stratosphere (Crutzen and Fishman, 1977; Cox and Burrows, 1979), its major importance arises from its high solubility in water. The latter ensures that a large fraction of gaseous H_2O_2 will be taken up in aqueous droplets. Over the past decade, evidence has accumulated that H_2O_2 dissolved in cloud, fog, and rainwater may play an important role, and in acidic droplets (i.e., pH $\lesssim 5$) even a dominant role, in the oxidation of SO_2 to H_2SO_4 (Hoffman and Edwards, 1975; Penkett et al., 1979; Dasgupta, 1980; Martin and Damschen, 1981; Graedel and Weschler, 1981; Chameides and Davis, 1982; Calvert and Stockwell, 1983; Brock and Durham, 1984; Hoffman and Jacob, 1984; Schwartz, 1984). Discussion of several proposed mechanisms for previous rate studies of the oxidation of S(IV) by H_2O_2 are beyond the scope of this document, but have recently been reviewed by several authors (e.g., Calvert, 1984). Hydrogen peroxide may also play a role in the oxidation of NO_2 dissolved in aqueous droplets, although relevant data are limited (Halfpenny and Robinson, 1952a,b; Anbar and Taube, 1954; Gertler et al., 1984) and additional research is required. In addition to the direct oxidation of SO_2 and NO_2 dissolved in aqueous droplets, the photolysis of H_2O_2 to produce aqueous OH radicals

$$(H_2O_2)_{aq} + h\nu \rightarrow 2(OH)_{aq} \qquad (5\text{-}39)$$

can lead to oxidation rates of S(IV) that can be competitive with calculated oxidation rates of S(IV) by $(H_2O_2)_{aq}$ and $(O_3)_{aq}$ (Chameides and Davis, 1982).

It should be emphasized, however, that substantial uncertainties remain concerning the quantitative role of H_2O_2 in acidification of aqueous particles and droplets (Richards et al., 1983). This is further complicated by the lack of reliable measurements of gas-phase H_2O_2 concentrations in the atmosphere, with the recognition that at least one important method for H_2O_2 analysis suffers from serious, previously unrecognized interferences (Zika and Saltzman, 1982; Heikes et al., 1982). Moreover, it has also been suggested recently that H_2O_2 may be formed in situ in aqueous droplets as the result of absorption of OH and HO_2 radicals and other precursors into solution from the gas phase (Graedel and Weschler, 1981; Heikes et al., 1982; Chameides and Davis, 1982).

5.3.7 Atmospheric Reactions of Formic Acid

As a gas-phase species, formic acid (HCOOH) cannot strictly be defined as a photochemical oxidant. Because it can be scavenged rapidly into water droplets, however, it can potentially function as an oxidant in cloud water and rain water. It can also be differentiated from other acids in that it is formed readily from the reactions of the Criegee intermediates discussed earlier and from the reaction of hydroperoxyl radicals with formaldehyde (Calvert and Stockwell, 1983). The formation of other acids may be orders of magnitude slower as the result of both the apparently lower rates of reaction of HO_2 radicals with the higher aldehydes and the much lower atmospheric concentrations of the higher aldehydes (Grosjean, 1982). Thus, formic acid is an example of a non-oxidant or weak oxidant in the gas phase, being transformed, upon incorporation in aqueous solutions, into an effective oxidizer of S(IV).

Formic acid (as well as acetic acid) has been identified among the acidic components of rain (Galloway et al., 1982). Although much uncertainty remains concerning the quantitative role of HCOOH and the higher organic acids, they potentially play a minor but still significant role in the acidification of rain.

5.4 TYPE REACTIONS OF OZONE AND PEROXYACETYL NITRATE IN SOLUTION

Polluted urban air contains a number of photochemical oxidants, including ozone, hydrogen peroxide, organic peroxides, singlet oxygen, peroxyacyl nitrates, and the various oxides of nitrogen (nitrogen dioxide, nitric oxide, etc.). Since these substances vary widely in their relative abundance, persistence, and reactivity with biological and nonbiological organic compounds, their importance in smog-related oxidative damage also varies. The oxides of nitrogen are found in high concentrations in polluted air and are the subject of a separate air quality criteria document (U.S. Environmental Protection Agency, 1982). Of the remaining compounds, the most important in terms of abundance and potential reactivity in biological receptors are ozone and peroxyacetyl nitrate (PAN). The purpose of this section is to provide a brief summary of the chemistry of the reactions in solution-phase chemistry of ozone and PAN with several of the more important types of functional groups found in organic molecules, particularly those functional groups that occur in molecules of biological interest.

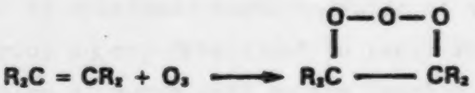
Type reactions of hydrogen peroxide are not given in this section. Evidence noted in section 5.3 and presented subsequently, in section 5.5, indicates that ambient air concentrations reported in the literature are likely to be overestimations of the true concentrations present.

5.4.1 Ozone

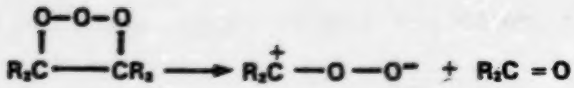
As noted in the previous section, ozone is a very powerful oxidizing agent and is capable of oxidizing most organic compounds, even alkanes, at room temperatures (Pryor et al., 1982). Despite its power as an oxidizing agent, ozone exhibits considerable selectivity in its reactions; that is, some functional groups are much more likely to be attacked and oxidized than are others. As an example, the relative reactivity in solution of four types of organic molecules with ozone has been reported by Pryor et al. (1982) to be: alkene, 400,000; sec-alcohol, 7.0; benzene (aromatic), 0.1; alkane(s), 0.01 to 1.0. The most reactive groups of interest are discussed below.

5.4.1.1 Alkenes. Alkenes are especially susceptible to oxidation by ozone. In fact, ozonolysis provides the basis for a standard test for identifying and locating the position of carbon-carbon double bonds in molecules. Double bonds occur in polyunsaturated fatty acids (PUFA) of the type that are found in biological lipids in cell membranes; and the reaction of ozone with PUFA has been studied in detail, since it is thought by some investigators that this process is responsible for a large part of the cellular damage caused by ozone (Pryor et al., 1976; 1981; 1982) (see chapter 10). The mechanism of the reaction of ozone with alkenes is very complex and not entirely understood. This area is the subject of a comprehensive review (Bailey, 1978).

The major reaction of ozone with non-hindered olefins is by a non-radical process first described by Criegee in the early 1950s. According to this scheme, ozone first reacts with the olefin by a 1,3-dipolar cycloaddition reaction to form an unstable 1,2,3-trioxolane (the primary ozonide in equation 5-40) that undergoes rapid decomposition to give the carbonyl oxide and an aldehyde or ketone (equation 5-41).

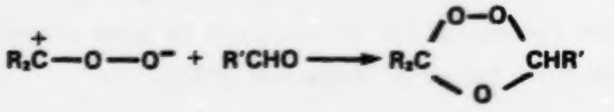


$$R_2C=CR_2 + O_3 \longrightarrow \begin{array}{ccc} O & - O - & O \\ | & & | \\ R_2C & - & CR_2 \end{array} \qquad (5\text{-}40)$$

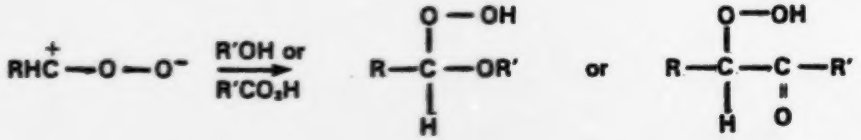


(5-41)

The reactions of the carbonyl oxide dictate the nature of the subsequent reactions. If the carbonyl compound formed in equation 5-41 is a reactive aldehyde, the carbonyl oxide and the aldehyde react to form the relatively stable 1,2,4-trioxolane (the ozonide in equation 5-42). If the carbonyl compound is a ketone, the carbonyl oxide dimerizes or polymerizes to yield a range of types of peroxidic compounds. The carbonyl oxide also reacts with active hydrogen compounds such as alcohols or acids to yield peroxidic products (equation 5-43) or with water to give acids or aldehydes as the ultimate products, as illustrated by equation 5-44. The reactions involving water also yield hydrogen peroxide, a species that can cause additional oxidative damage.

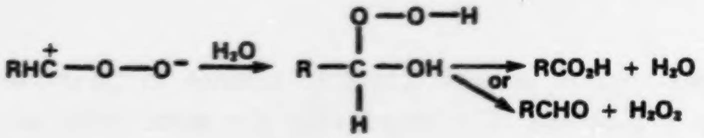


(5-42)



$$\mathrm{RH\overset{+}{C}-O-O^{-}} \xrightarrow[\mathrm{R'CO_2H}]{\mathrm{R'OH\ or}} \mathrm{R-\underset{H}{\overset{O-OH}{C}}-OR'} \quad \text{or} \quad \mathrm{R-\underset{H}{\overset{O-OH}{C}}-\underset{O}{\overset{}{C}}-R'}$$

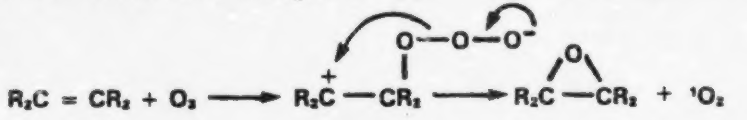
(5-43)



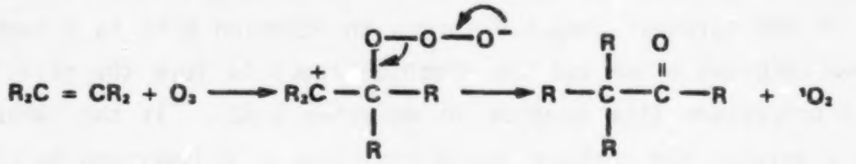
$$\mathrm{RH\overset{+}{C}-O-O^{-}} \xrightarrow{\mathrm{H_2O}} \mathrm{R-\underset{H}{\overset{O-O-H}{C}}-OH} \longrightarrow \mathrm{RCO_2H + H_2O} \;\text{ or }\; \mathrm{RCHO + H_2O_2}$$

(5-44)

Most non-radical reactions of alkenes with ozone proceed through reactions similar to the ones described above and generally result in the ultimate cleavage of the double bond. If the double bond, however, is substituted with bulky substituents and is sterically hindered, these cleavage products become less dominant and the formation of epoxides or other partial cleavage products becomes more dominant (equations 5-45 and 5-46). The molecular oxygen released in equations 5-45 and 5-46 is in the form of singlet oxygen, which can itself cause further oxidative damage.

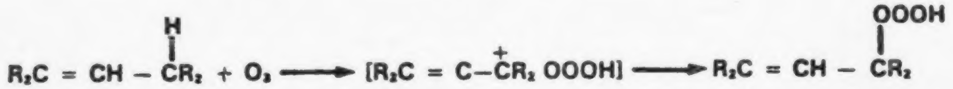


$$R_2C=CR_2 + O_3 \longrightarrow R_2\overset{+}{C}-\underset{}{\overset{O-O-O^-}{\overset{|}{C}}}R_2 \longrightarrow R_2C\overset{O}{-}CR_2 + {}^1O_2 \qquad (5\text{-}45)$$

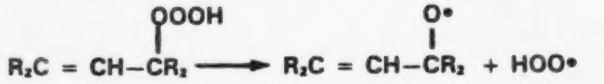


$$R_2C=CR_2 + O_3 \longrightarrow R_2\overset{+}{C}-\underset{\overset{|}{R}}{\overset{O-O-O^-}{\overset{|}{C}}}-R \longrightarrow R-\underset{\overset{|}{R}}{\overset{R}{\overset{|}{C}}}-\overset{O}{\overset{\parallel}{C}}-R + {}^1O_2 \qquad (5\text{-}46)$$

For most alkenes, non-radical pathways of ozone oxidation dominate. Ozone also reacts, however, with alkenes to produce free radicals. Even though free-radical-generating pathways of reaction are minor when compared to Criegee ozonolysis, these reactions may result in significant damage since they can initiate autoxidation, which is a chain reaction. A suggested mechanism (Pryor et al., 1982) for this type of reaction involves hydride abstraction of an allylic hydrogen with ion recombination in the cage to give a hydrotrioxide, which then decomposes to form radicals (equation 5-47).



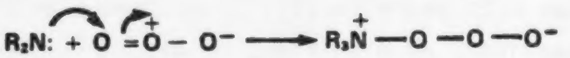
$$R_2C=CH-\overset{H}{\overset{|}{C}}R_2 + O_3 \longrightarrow [R_2C=C-\overset{+}{C}R_2\,OOOH] \longrightarrow R_2C=CH-\overset{OOOH}{\overset{|}{C}}R_2$$

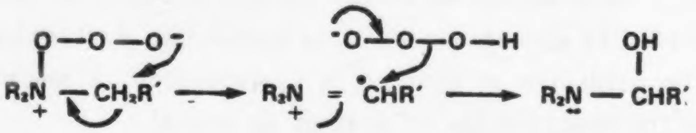


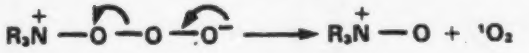
$$R_2C=CH-\overset{OOOH}{\overset{|}{C}}R_2 \longrightarrow R_2C=CH-\overset{O\bullet}{\overset{|}{C}}R_2 + HOO\bullet \qquad (5\text{-}47)$$

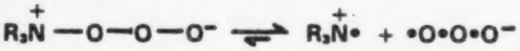
5.4.1.2 Amines. Amines are, in general, close to alkenes in their reactivity toward ozone, although protection is afforded when the amino group exists as an amide or salt, both of which are less susceptible to oxidation by ozone. Whereas ozone acts as a 1,3-dipole in its reaction with alkenes, its attack on amines is as an electrophile (equation 5-48). In general, ozone attack on amines is by three competing reactions: (1) side chain oxidation (equation

5-49); (2) amine oxide formation and transformations to nitro compounds (equation 5-50); and (3) dissociation to the nitrogen cation radical and ozonate anion radical (equation 5-51) and the subsequent reaction of these radical species (Bailey, 1982). Reaction 5-50 is important for primary and tertiary amines, although in the case of primary amines the amine oxide formed is unstable and undergoes further reactions. Reaction 5-51 is important mainly for primary amines, while reaction 5-49 occurs with all amines bearing primary alkyl groups. Reaction 5-52, in which radicals are produced, is important for secondary amines. Reaction 5-52 also results in the formation of superoxide.


(5-48)

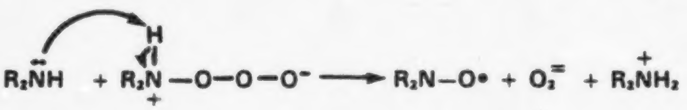

(5-49)


(5-50)

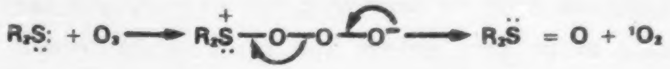


$$R_3\overset{+}{N}-O-O-O^- \rightleftharpoons R_3\overset{+}{N}\bullet + \bullet O \bullet O \bullet O^-$$

(5-51)


(5-52)

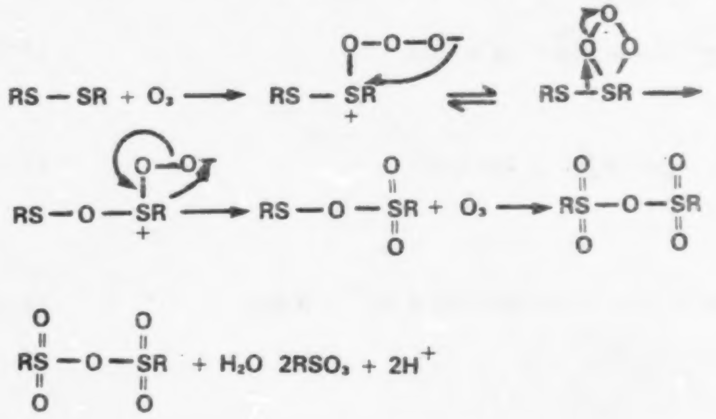
5.4.1.3 Sulfur Compounds. Like amines, sulfur compounds also undergo an initial electrophilic attack by ozone (Bailey, 1982). Ozone reacts with sulfides such as methionine to produce both sulfoxides and sulfones. The ractivity of the sulfides decreases as the electron-withdrawing power of the groups attached to the nucleophilic sulfur center increases. The mechanism for the oxidation of a sulfide to the sulfoxide involves electrophilic ozone attack on the sulfur, followed by loss of oxygen to give the sulfoxide (equation 5-53). A slower similar reaction then converts the sulfoxide to the sulfone. A number of researchers have reported that less than 2:1 mole ratios of ozone to sulfide are required for the sulfide-to-sulfone reaction and that the more reactive the sulfide, the less ozone is required. One possible explanation for these facts is that the oxygen evolved in reaction 5-53 is singlet oxygen, which could oxidize additional sulfide molecules.



$$R_2\ddot{S}: + O_3 \longrightarrow R_2\overset{+}{S}{-}O{-}O{-}O^- \longrightarrow R_2\ddot{S} = O + {}^1O_2 \qquad (5\text{-}53)$$

While the main reaction of ozone with sulfides is apparently the attack on sulfur with loss of oxygen to yield a sulfoxide, side-chain oxidationand sissociation to sulfur cation radicals and the ozone anion radical also can occur, although to a lesser extent than the analogous amine-ozone reactions.

Dissulfides undergo reaction with ozone to yield, in aqueous solution, sulfonic acids, although the reactivity of disulfides is 40 to 50 times less than that of thioethers. The proposed mechanism for the reaction of disulfides is shown in equation 5-54. In agreement with this mechanism, Previero et al. (1964) have reported the oxidation of cystine to cysteic acid, a reaction of potential importance in the inactivation of enzymes by ozone.

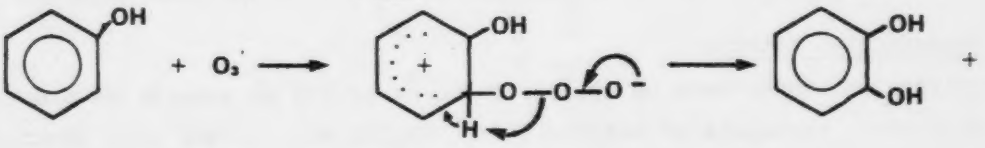


$$RS(O_2){-}O{-}S(O_2)R + H_2O \; 2RSO_3 + 2H^+ \qquad (5\text{-}54)$$

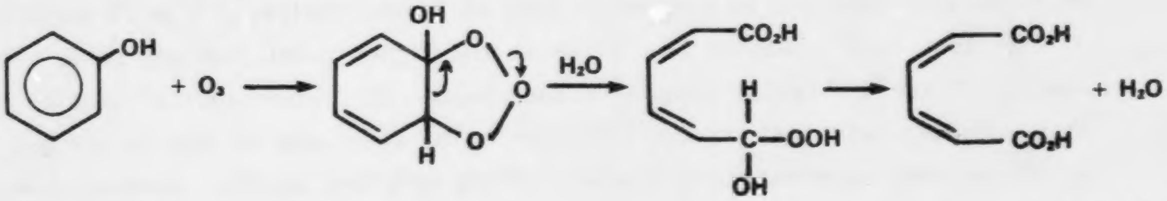
Thiol groups are the most reactive of the sulfur functional groups, having reactivities similar to those of isolated olefinic double bonds. The reaction products for the attack of ozone on sulfhydryls are generally sulfonic acids, although oxidation to the disulfide also has been reported (Mudd et al., 1969). Since many enzymes rely on active cysteine residues for their catalytic activity, sulfhydryl oxidation is a major mechanism for enzyme inactivation by ozone.

5.4.1.4 Aromatics. The benzene ring is much less reactive toward ozone than is the olefinic double bond. In solutions containing both olefinic and aromatic unsaturation, ozone absorption is usually rapid until the olefinic bonds have entirely reacted, after which absorption becomes much slower. In compounds containing both aromatic and olefinic portions, such as the indole ring of tryptophan, the initial ozone attack occurs exclusively at the olefinic part of the molecule. Benzenes and substituted benzenes do, however, react with ozone, although slowly, with glyoxals and simple carboxylic acids reported as the major products. Phenol has also been reported as a minor product from benzene oxidation. The mechanisms for benzene ozonation are not known and are difficult to study since the initial products are primarily olefinic and undergo further ozonation reactions quite rapidly.

Phenol is somewhat more reactive toward ozone than benzene is and there has been more interest in the ozonation of phenols than in any other benzene derivatives because of the need to purify wastewater containing these compounds. The initial attack of ozone on phenol probably involves both hydroxylation to yield catechol (equation 5-55) and bond cleavage to give muconic acid (equation 5-56) (Yamamoto et al., 1979). Both of these products undergo further ozonations, producing formic acid and carbon dioxide as the ultimate products from reaction of phenol.

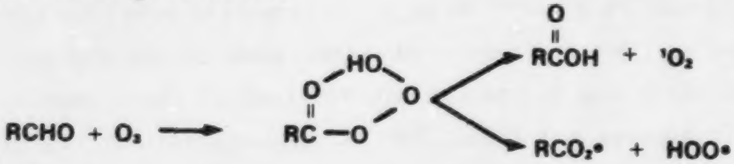


(5-55)



(5-56)

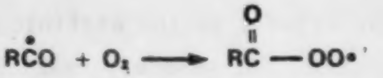
5.4.1.5 Aldehydes and Ketones. Aldehydes can react with ozone without the involvement of oxygen (equation 5-57a), or ozone can initiate aldehyde autoxidation (equations 5-57b, and 5-58 through 5-60). In either case, the initial reaction produces acyl hydrotrioxides followed by decomposition to peroxides and carboxylic acids.



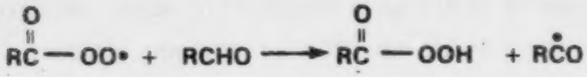
(5-57a)

(5-57b)

$$RCO_3\bullet + RCHO \longrightarrow RCO_3H + RC\dot{O} \qquad (5\text{-}58)$$



$$R\dot{C}O + O_2 \longrightarrow \overset{O}{\overset{\|}{RC}}-OO\bullet \qquad (5\text{-}59)$$



$$\overset{O}{\overset{\|}{RC}}-OO\bullet + RCHO \longrightarrow \overset{O}{\overset{\|}{RC}}-OOH + R\dot{C}O \qquad (5\text{-}60)$$

Simple ketones react only very slowly, if at all, with ozone. Ketones that do react give carboxylic acids as the main products.

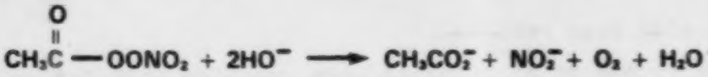
Some of the possible reactions of ozone with important functional groups have been described above. It should be remembered, however, that ozone is capable of reacting with most organic molecules, even alkanes, although many of these reactions are too slow to be important in the biosphere. Under some conditions, however, ozone is converted into other oxidizing species. For example, at pH greater than 9 in aqueous solution, ozone is rapidly converted to hydroxyl radicals ($HO^{\bullet}$) that are less selective than ozone and react more rapidly with organic substances in many cases (National Academy of Sciences, 1977). The conversion of ozone to superoxide ($O_2\cdot$) also has been reported.

5.4.2 Peroxyacetyl Nitrate

Peroxyacyl nitrates make up another group of oxidizing substances present in polluted air. Peroxyacetyl nitrate (PAN), $CH_3COO_2NO_2$, is the most abundant of these compounds and is present in smog at levels typically 5 to 20 percent of the ozone level (chapter 6). Since at the higher levels PAN may cause crop damage and eye irritation (chapter 7 and chapter 11), toxicological studies on this compound have been fairly extensive. The chemistry of PAN in the gas phase has been examined in a number of smog modeling studies; however, the literature on the chemistry of PAN in solution, particularly in aqueous solution, is not extensive. Most of the chemical studies to be described are included in a review published in 1976 (Mudd, 1976).

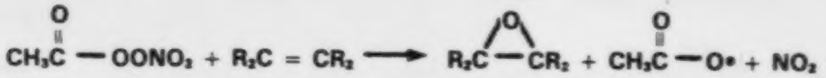
While PAN is relatively stable in the gas phase, in alkaline aqueous solution it undergoes ready decomposition with quantitative formation of nitrite ion (equation 5-61). Although the mechanistic details of this decomposition are not fully understood, it appears to be a nucleophilic substitution reaction that does not involve free radicals. At least some of the oxygen produced is singlet oxygen, which may be responsible for some of the oxidative reactions of PAN. In acidic aqueous solutions, PAN is somewhat soluble (Henry's

Law coefficient of 5 at 10°C) and decomposes to nitrate, nitrite, and organic fragments at a temperature-dependent rate (Holdren et al., 1984). The oxidation of a number of molecular species by PAN has been examined and some of these reactions are summarized below.

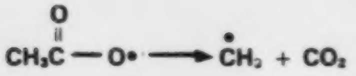


$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OONO_2 + 2HO^- \longrightarrow CH_3CO_2^- + NO_2^- + O_2 + H_2O \qquad (5\text{-}61)$$

5.4.2.1 Alkenes. Alkenes are oxidized by PAN to epoxides with the production of methyl nitrite and nitromethane by a reaction pathway suggested to involve free radicals (equations 5-62 through 5-64).



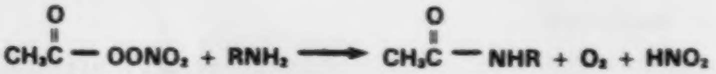
$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OONO_2 + R_2C=CR_2 \longrightarrow R_2C\overset{O}{-}CR_2 + CH_3\overset{\overset{\displaystyle O}{\|}}{C}-O\bullet + NO_2 \qquad (5\text{-}62)$$



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-O\bullet \longrightarrow \dot{C}H_3 + CO_2 \qquad (5\text{-}63)$$

$$NO_2 + \dot{C}H_3 \longrightarrow CH_3NO_2 \text{ and } CH_3ONO \qquad (5\text{-}64)$$

5.4.2.2 Amines. Primary amines have been reported (Wendschuh et al., 1973) to react rapidly with PAN to yield acetamides and nitrous acid (equation 5-65). The reaction of PAN with tertiary amines yields an unknown product that produces chemiluminescence at λ = 660 nm.



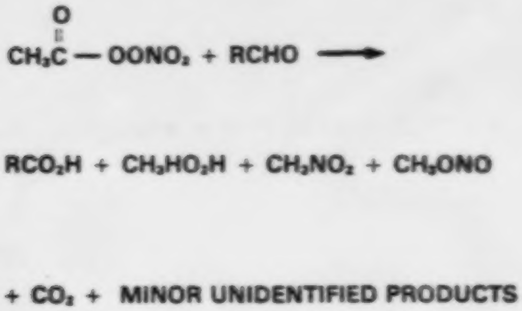
$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OONO_2 + RNH_2 \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}-NHR + O_2 + HNO_2 \qquad (5\text{-}65)$$

5.4.2.3 Sulfur Compounds. Methionine is oxidized by PAN to methionine sulfoxide but with production of only negligible amounts of methionine sulfone. The mechanism for this reaction has not been determined. The formation, however, of free radicals has been suggested in the oxidation of dimethyl sulfide to dimethyl sulfoxide in nonaqueous solution.

Disulfides react with PAN, although, in general, rather slowly, with large excesses of PAN required for the reactions. The products from cystine oxidation consist of cysteic acid along with trace amounts of cystine-S,S-dioxide.

Thiols are very reactive toward PAN. In the case of cysteine, two moles react per mole of PAN to produce disulfide. The reactivity is pH-dependent, increasing greatly as the pH is raised, which suggests that RS^- is the reactive species rather than RSH. The formation of S-acetyl products from the reaction of PAN with thiols has also been reported.

5.4.2.4 Aldehydes. Wendschuh et al. (1973a) have reported that the addition of an aldehyde to organic solutions of PAN results in the oxidation of the aldehyde to the corresponding acid in approximately an 85 percent yield (equation 5-66).



$$CH_3\overset{O}{\overset{\|}{C}}-OONO_2 + RCHO \longrightarrow RCO_2H + CH_3HO_2H + CH_3NO_2 + CH_3ONO + CO_2 + \text{MINOR UNIDENTIFIED PRODUCTS} \qquad (5\text{-}66)$$

The reaction occurs at an increased rate for aldehydes with electron-donating R groups. The reaction is first order in PAN but the stoichiometry of reaction is not simple, with one to three moles of aldehyde consumed for each mole of PAN reacted. The aiuthors suggest a free-radical pathway initiated by PAN as the most likely reaction mechanism.

Knowledge concerning the colution chemistry of peroxyacyl nitrates is quite limited. It is known, however, that PAN reacts with many biochemically important functional groups. The half-life of PAN in water is fairly short, about 4.4 minutes at pH 7.2; therefore, PAN itself may not be able to react with susceptible biological molecules before decomposition occurs, except perhaps locally at the site of initial deposition or impact. The decomposition products of PAN include nitrite ion and singlet oxygen, however, both of which can cause oxidative damage. Thus, some of the toxicological effects of PAN should possibly be attributed to the products of the decomposition of PAN in an aqueous environment.

5.5 SAMPLING AND MEASUREMENT OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

5.5.1 Introduction

Since the publication at the beginning of this decade of the first air quality criteria document on ozone and other photochemical oxidants (1970), there have been significant changes in the technology associated with measurement of these pollutants in ambient air.

The chemiluminescent reaction of ozone (O_3) with ethylene has been used successfully as the basic working principle in instrumentation whose response is both specific for O_3 and is linear with O_3 concentrations over the range usually found in ambient air. In general, chemiluminescence analyzers have significantly improved both the time resolution and the ease with which monitoring for ozone can be routinely carried out.

Advances in electronics technology have allowed development of ultraviolet absorption photometers of adequate precision for determining atmospheric concentrations of O_3. The principle of the ultraviolet photometry has also been applied to a new standard calibration procedure for O_3 instruments. The possible effect on the measurement of ambient O_3 concentrations of this recent change in calibration procedure is discussed in this section. Improved understanding of photochemical systems has resulted in an interest in the fate of organic nitrogen species and of hydrogen peroxide in ambient atmospheres, such that researchers have undertaken the development of refined methods for the measurement of peroxyacyl nitrates and of hydrogen peroxide.

This section will describe analytical techniques for measurement of ozone and other photochemical oxidants. Primary emphasis will be given to those techniques presently considered most satisfactory for routine monitoring. Since the original criteria document for photochemical oxidants emphasized continuous methods for measuring "total oxidants," these techniques will also be discussed briefly in order to place past measurements in perspective. For the same reason, the relationship between measurements of ozone and total oxidants will also be discussed.

In addition to developments in analytical techniques, EPA has codified and instituted a formal nationwide program of quality assurance in the routine operation of monitoring pollutants in ambient air. Some examples of these procedures will be documented in this section as they apply to actual operation of the analytical instrumentation. A detailed description of analytical procedures, quality assurance procedures, and reporting requirements are contained in Quality Assurance Handbook for Air Pollution Measurement Systems (U.S. Environmental Protection Agency, 1977). Pertinent rules and regulations are contained in the Federal Register (U.S. Environmental Protection Agency, 1979a; 1979b; 1979c).

An appreciation of some of the errors involved in present monitoring techniques is important in evaluating the quality of ambient pollution data. Three types of errors are discussed in this section: interferences, systematic errors, and random errors.

The measurement of individual pollutants in ambient air is complicated by the presence of other airborne chemicals that may produce responses in the measuring apparatus generally indistinguishable from those produced by the pollutant being monitored. These spurious responses are known as "interferences." Extensive tests are conducted by the U.S. Environmental Protection Agency and other laboratories, or both, on potential interferences in proposed measurement techniques before they are considered suitable for routine monitoring. In addition, researchers engaged in methods development or application investigate interferences before reporting such methods in the literature. This section describes reported interferences for the routine methods listed. It should be noted, however, that not all potential interferences have equal significance. Their magnitude will, in general, depend on the ambient concentrations of the interfering species, the inherent sensitivity of a given procedure to spurious responses, and, in some cases, on details of the measuring apparatus that may vary from instrument to instrument. An analytic technique sensitive to interference may still be useful if the interfering species occurs only in low concentrations in ambient air or may otherwise be accounted for.

In addition to errors introduced by interferences, a given analytic technique may be subject to systematic over- or underestimation of the pollutant concentration, which affects the accuracy with which these concentrations are known. Such errors are known as "biases." The assessment of the magnitude of such biases for a given analytical method generally requires extensive testing, often by a number of laboratories sampling the same pollutant concentration in ambient air (collaborative testing).

Random errors introduced by unknown factors such as variability in detailed procedures used by different operators or sensitivity of the method to small uncontrollable variations in operational parameters are generally known collectively as the imprecision of the method. A measure of this type of error often used is the standard deviation of a set of measurements. The precision of a method is also often assessed in collaborative testing procedures. The results of testing for these two error types are described in this section where they are available.

5.5.2 Quality Assurance in Ambient Air Monitoring for Ozone

Quality assurance as defined by EPA rules and regulations consists of two distinct functions. One is the assessment of the quality of monitoring data by estimating their precision and accuracy. The other is the control and possible improvement, depending on the results of the first function, of the quality of the ambient air data by implementation of quality control policies, procedures, and corrective actions.

Each quality control program, developed by the individual States and approved by the EPA Regional Administrator, must include operational procedures for each of the following activities:

1. Selection of methods, analyzers, or samplers (prescribed reference and equivalent methods for ambient air monitoring are described elsewhere in this chapter);
2. Installation of equipment;
3. Calibration--Test concentrations for ozone must be obtained by means of the ultraviolet (UV) photometric calibration procedure described elsewhere in this chapter or by means of a certified ozone transfer standard; permeation tubes for NO_2 must be working standards that can be compared to Standard Reference Material (SRM) from the National Bureau of Standards.
4. Zero/span checks and adjustments of automated analyzers;
5. Control checks and their frequency;
6. Control limits for zero, span, and other control checks, and respective corrective actions when such limits are surpassed;
7. Calibration and zero/span checks for multiple range analyzers;
8. Preventive and remedial maintenance;
9. Quality control procedures for air pollution episode monitoring;
10. Recording and validation of data;
11. Documentation of quality control information.

A one-point precision check must be carried out at least every 2 weeks on each automated analyzer used for ozone, using a precision test gas of known concentration. Each calendar quarter, at least 25 percent of the analyzers used by the State and Local Air Monitoring Stations (SLAMS) for monitoring ozone must be formally audited by an independent operator by challenging with at least one audit gas of known concentration in each of the four concentration ranges. Similar requirements are set forth for monitoring networks designed to assess Prevention of Significant Deterioration (PSD) requirements.

In addition to requirements and recommendations associated with the selection, installation, and maintenance of monitoring equipment, the above-cited Federal Register publications discuss certain design criteria for monitoring networks (SLAMS and the National Aerometric Monitoring Stations, NAMS: see chapter 6). Included are requirements on siting of monitors in order to obtain ozone concentrations that are representative of regions of varying dimensions. For example, a "middle scale" monitor would represent conditions close to sources of NO_x such that local ozone scavenging effects might be of significance. A "neighborhood scale" monitor, on the other hand, would be located somewhere in a reasonably homogeneous urban subregion having dimensions of a few kilometers. Other "scales" applicable to siting of ozone monitors include urban scale, which would be used to estimate concentrations characteristic of an area having dimensions between several and 50 kilometers or to measure high concentrations downwind of an area with high precursor emissions; and regional scale, used to typify concentrations over portions of a major metropolitan complex up to dimensions of hundreds of kilometers. For ozone SLAMS stations, applicable scales are middle, neighborhood, urban, and regional. Requirements for NAMS stations for ozone are neighborhood and urban scale. Two ozone NAMS stations are expected to be sufficient for each urban area: one for specific transport conditions leading to high ozone; and the other for monitoring peak concentrations relative to population exposure.

5.5.3 Sampling Factors in Ambient Air Monitoring for Ozone

Sampling factors may have a crucial effect on the quality and utility of measurements both in ambient air and in controlled laboratory situations. Sampling techniques and strategies must preserve the integrity of a representative fraction of ambient air and must be consistent with the specific purpose of the measurement. In this section, the significance of some sampling factors will be discussed briefly. For more detailed discussions of this subject, the reader is referred to Ott (1977) and to reports prepared for EPA by the National Academy of Sciences (Standing Air Monitoring Work Group, 1977; (National Academy of Sciences, 1977a; National Academy of Sciences, 1977b).

5.5.3.1 Sampling Strategies and Air Monitoring Needs. Air monitoring data relevant to assessing ambient O_3 or oxidant levels are collected for a variety of specific needs, including:

1. Data to be used in trend analysis as indicators of the state of attainment of ambient air quality standards.
2. Data to be used in development of O_3 control strategies and evaluation of their effectiveness.
3. Data to be used in the development and validation of air quality simulation models capable of application to the O_3 problem.
4. Data to be used in investigation of causes of the ozone problem both in general and in specific localities.
5. Data to be used in special research studies such as the effects of ambient air pollution on human health and welfare.

Each specific purpose or need requires special considerations in designing a suitable air sampling strategy. For example, several years of O_3 data might be required for the adequate assessment of trends that resulted from the application of a particular control strategy rather than trends that resulted from chance local meteorological conditions. In contrast, the validation of an air quality simulation model might require only a few carefully chosen days of very detailed measurements of O_3, hydrocarbons, and NO_x, as well as detailed meteorological data and time-varying emissions along the trajectory of the air parcel in question.

5.5.3.2 Air Monitoring Site Selection. Ozone in the lower troposphere is a product of photochemical reactions that involve sunlight, hydrocarbons, and oxides of nitrogen. In typical urban atmospheres, ozone precursors react to produce ozone at such a rate that the O_3 reaches its daily peak level in the middle of the day at locations downwind from the source-intensive center-city area. Thus, if peak O_3 concentrations are to be measured, monitoring stations should, in general, be located downwind from city centers. This downwind distance may be on the order of 15 to 30 kilometers (9 to 19 miles), depending on predominant wind patterns in the area (Standing Air Monitoring Work Group, 1977). It should be emphasized, however, that this distance may be highly area-specific. A study (Wolff and Lidy, 1978) of emissions originating in the Houston area suggested that, in this case, the distance may be considerably greater than the figures quoted above.

Once a station is located, additional sampling considerations arise because of the chemical reactivity and instability of the O_3 molecule. Ozone reacts extremely rapidly with NO and with some hydrocarbon compounds, including most of those emitted by vegetation. Also, O_3 decomposes readily on contact with the surface of many materials. Consideration of these effects led to the development of specific criteria for locating an O_3 monitoring station (Standing Air Monitoring Work Group, 1977; National Academy of Sciences, 1977b). Briefly, the inlet of the sampling probe of the ozone analyzer should be positioned 3 to 15 meters (10 to 49 feet) above ground, at least 4 meters (13 feet) from large trees, and 120 meters (349 feet) from heavy automobile traffic. Sampling probes should be designed so as to minimize O_3 destruction by surface reaction or by reaction with NO.

Another consideration that has significance for the selection of sites for air monitoring stations is the fact that ambient monitoring data, as routinely obtained, have limited validity as absolute measures of air quality. This limitation arises from the fact that, at ground level, the ambient atmosphere is inhomogeneous as a result of a continuous influx of fresh emissions, incomplete mixing, and destruction of O_3 by fresh and unreacted emissions and destruction on surfaces. In view of such inhomogeneity, monitoring data from a fixed network provide measures of air quality at a discrete number of locations but may not detect temporal and spatial variations in ozone concentrations of a localized nature. This problem can be alleviated by use of a greater density of monitoring stations or by use of a validated air quality model. Such models are capable of helping quantify the emission, dispersion, and chemical reaction processes. Their outputs can provide data on the distribution of air quality concentrations between widely spaced ambient monitors.

The emphasis in this section has been on a brief discussion of sampling strategies. The word sampling is also widely considered to mean those techniques that are required to obtain a parcel of air that is representative of the polluted atmosphere, and to maintain its integrity until a measurement of concentration has been carried out. Considerations relating to this meaning of sampling are discussed as appropriate in the following sections on measurement techniques.

5.5.4 Measurement Methods for Total Oxidants and Ozone

5.5.4.1 Total Oxidants. Although ozone was first unambiguously identified in polluted atmospheres by spectroscopic techniques (Stephens et al., 1956), the earliest procedures for routinely monitoring O_3 and other oxidizing species in the atmosphere were based on iodometry. Iodometric techniques are inherently non-specific in that a variety of oxidizing species in addition to O_3 may be positive interferences, producing iodine in solution; whereas reducing agents are negative interferences. Thus, the name "total oxidants" was coined because the technique responded not only to O_3 but to other oxidants such as peroxides, peroxyacetyl nitrate (PAN), and nitrogen dioxide (NO_2). Total oxidants are then actually defined by the particular iodometric procedure used, since the response to the various oxidizing species present will depend on the details of the procedure. This will be more evident when interferences are discussed below. The use of the word "total" is in itself a misnomer. The measurement does not reflect a sum of the oxidizing species present because the various oxidants present in the atmosphere react to produce iodine at different stoichiometries and different rates. In spite of these difficulties, the measurement of total oxidants was a useful method for characterization of the atmosphere because of its correlation with the principal oxidant, O_3; and, consequently, there is a large oxidant data base available. For these reasons, the two principal methods used for monitoring total oxidants are discussed in more detail below.

The bulk of the total oxidants data base was obtained by the use of two types of continuous monitoring instruments. In both types, an air sample is continuously scrubbed by an aqueous reagent containing potassium iodide (KI). In colorimetric oxidant instruments, the iodine is measured photometrically by ultraviolet absorption. In the other common type instrument, the iodine produced is measured by electrochemical means. Both of these instruments are discussed and compared in more detail below. Many other chemical techniques for oxidants have been proposed and in some cases applied, but for these reference is made to the original literature (Hodgeson, 1972a; Katz, 1976).

The first colorimetric analyzers were patterned after the instrument described by Littman and Benoliel (1953). In this and the commercial versions, the air sample flow and the liquid reagent flow were mixed countercurrently in a contacting column. The reagent contained 20 percent KI (later 10 percent) and was maintained at pH = 6.8 with a phosphate buffer. Ozone and other oxidants produce iodine according to the reaction:

$$O_3 + 3I^- + H_2O = I_3^- + O_2 + 2OH \qquad (5\text{-}67)$$

The tri-iodide ion exhibits an intense absorption maximum at 352 nm, which is used to monitor continuously the I_3^- concentration. These instruments operate over a range of about 0.01 to 1 ppm and have a 90 pecent full-scale response time of a few minutes. Interferences and compensation for them are discussed below.

The electrochemical oxidant sensors are more correctly called amperometric sensors in that an electrochemical current is measured rather than an absolute transfer of charge. Two types of electrochemical cells have been used, an electrolytic cell (Brewer and Milford, 1960; Mast and Saunders, 1962) and a galvanic cell (Hersch and Deuringer, 1963). Of these, the Brewer cell has been by far the most frequently used in the commercial Mast Meter version. In the Brewer cell, sample air and reagent (2 percent KI, 5 percent KBr buffered at pH = 6.8 with phosphate buffer) flow concurrently over a wire helix cathode. A polarization voltage of 0.24 volt applied between the cathode and anode produces a thin layer of hydrogen at the cathode and a small but constant polarization current that represents zero O_3 concentration. Ozone absorbed in solution produces the tri-iodide ion, which reacts with and removes hydrogen, temporarily depolarizing the cathode. A current to repolarize the cathode then flows through the external circuit. The magnitude of this differential current is proportional to the hydrogen removed and is recorded as a function of O_3 concentration. If contact efficiences were 100 percent and reaction stoichiometries well-established, the absolute coulometric current should be equivalent to the concentration of O_3 absorbed. In practice, it is necessary to calibrate these analyzers with standard O_3 samples (see below). The coulometric yield of the Brewer cell has been reported to be about 75 percent (Wartburg et al., 1964). The normal operating range for the Brewer cell in atmospheric monitoring is 0.01 to 1 ppm, but these sensors will also work at higher concentrations.

The interferences for both colorimetric and amperometric O_3 analyzers are other oxidizing and reducing species in the atmosphere. The major oxidant in ambient air by far is O_3 (chapter 6); and the other oxidants present, except

NO_2, are considered part of the total oxidants measured rather than interferences. The dominant reducing interference is SO_2. Thus, the major interferences present in ambient air and considered below are NO_2 and SO_2.

The magnitude of the NO_2 interference is variable and depends upon contact design and KI concentration (Tokiwa, 1972; Intersociety Committee, 1970). For the Brewer amperometric cell, the interference from NO_2 is only 6 percent of an equivalent concentration of O_3 (Tokiwa, 1972), presumably because of the low KI concentration and short contact time. For the colorimetric oxidant analyzer, NO_2 interference equivalents are about 20 percent for 10 percent KI solution and vary from 20 to 32 percent for 20 percent KI depending on O_3 concentration (Tokiwa, 1972). The method used for compensating for NO_2 interference is simultaneous measurement of NO_2 and correction of the corresponding oxidant reading. For this reason, the terms "corrected" or "adjusted" oxidant are often used.

The interference from SO_2 is quantitative for both colorimetric and electrochemical oxidant measurements, with one mole of SO_2 consuming one mole of tri-iodide ion. If the SO_2 concentration is less than that of total oxidant and SO_2 is simultaneously measured, the "adjusted" oxidant reading may also contain a correction for SO_2. This was the procedure previously applied in the older aerometric data for California, where SO_2 levels were inherently low because of low-sulfur fuel requirements. For many areas of the East Coast and Midwest, such a correction was not possible and preferential SO_2 scrubbers were used. The most common of these consisted of chromium trioxide impregnated on glass fiber filters (Saltzman and Wartburg, 1965) or an inert chromatography support (Mueller et al., 1973). These scrubbers may be effective in the hands of skilled operators but their use is not without problems. Among these problems are partial oxidation of NO to NO_2 and of H_2S to SO_2, and partial removal of O_3 when the scrubber is wet or contaminated (Hodgeson, 1972a).

5.5.4.2 Ozone

5.5.4.2.1 Gas-phase chemiluminescence. Many of the O_3 oxidation reactions are sufficiently energetic that they produce electronically excited products, intermediates, or reactants, which in turn may chemiluminesce (Zocher and Kautsky, 1923; Bowman and Alexander, 1966). Although well known for many years, such reactions were not applied to chemical analysis until the 1960s. In 1965, Nederbragt reported a detector that employed chemiluminescence from the reaction of O_3 with ethylene for measurement of O_3 in the vicinity of large accelerators (Nederbragt et al., 1965; Warren and Babcock, 1970).

Applications to atmospheric analysis were a natural consequence (Stevens and Hodgeson, 1973). When it promulgated the first standards for the criteria pollutants in 1971 (U.S. Environmental Protection Agency, 1971a), EPA also published reference methods for measurement of these pollutants. The reference method for O_3 to be used by EPA and the states for determining compliance was the O_3-ethylene chemiluminescence method. Appendix D of 40 CFR, Part 50, describes the principle of the method, including a method of calibration (U.S. Environmental Protection Agency, 1971b). Since then, the measurement principle has remained the same but calibration procedures have undergone extensive revision as discussed below (section 5.5.5). It is also noteworthy that the reference method is specific for O_3, whereas the data used for establishing the standard were based on measurement of total oxidants. This issue is addressed in section 5..

A flow of sample air (1 to 5 L/min) containing O_3 and a small flow of pure ethylene are mixed at atmospheric pressure in a small reaction chamber closely coupled to the photocathode of a photomultiplier tube. The reaction between O_3 and ethylene produces a small fraction of electronically excited formaldehyde. Chemiluminescence from this excited state results in a broad emission band centered at 430 nm (Finlayson et al., 1974). The emission intensity that is monitored is a linear function of O_3 concentration from 0.001 to greater than 1 ppm. The relation between intensity and concentration; i.e., instrument calibration, must be determined for each instrument with standard concentrations of O_3 in air. The minimum detection limit and the response time are functions of detector design. Detection limits of 0.005 ppm and response times of less than 30 seconds are readily attained, however, with modest design features. For example, cooling the photomultiplier improves the sensitivity but is not normally required. There are no known interferences among the common atmospheric pollutants. There have been reports of a positive interference when O_3 is measured in the presence of water vapor; i.e., a signal enhancement of 3 to 12 percent in high humidity as opposed to measurement of the same concentration of O_3 in dry air (California Air Resources Board, 1976). Where this may be a real problem, it can be minimized by performing calibrations with humidified air. Finally, in order to obtain acceptable measurement precision and constant span, analyzers must contain means for maintaining constant air and ethylene flow rates.

Under Title 40, Code of Federal Regulations, Part 53, EPA has published ambient air monitoring reference and equivalent methods (U.S. Environmental

Protection Agency, 1975). This regulation prescribes methods of testing and performance specifications that commercial analyzers must meet in order to be designated as a reference method or as an equivalent method. An analyzer may be designated as a reference method if it is based on the same principle as the reference chemiluminescence method and meets performance specifications. An automated equivalent method must meet the prescribed performance specifications and show a consistent relationship with a reference method. These specifications for O_3 analyzers are listed in Table 5-7. Commercial analyzers that have been designated as reference or equivalent methods are listed in Table 5-8. Information concerning the applications supporting the designation of analyzers as reference or equivalent methods may be obtained by writing the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Research Triangle Park, NC 27711.

5.5.4.2.2 Gas-solid chemiluminescence. The first chemiluminescence technique for O_3 was developed by Regener for stratospheric measurements (Regener, 1960) and later for measurements in the troposphere (Regener, 1964). The chemiluminescence was obtained from the reaction of O_3 with Rhodamine-B adsorbed on activated silica gel. The emission is in the red region of the visible and is characteristic of the fluorescence spectrum of Rhodamine-B. The intensity is a linear function of O_3 concentration, the minimum detection limit can be lower than 0.001 ppm, and no atmospheric interferences have been observed (Hodgeson et al., 1970). The technique is, in fact, more sensitive than the gas-phase Nederbragt method and does not require critical control of flow rate. It had the disadvantage in the original analyzer built, however, that frequent and periodic internal calibration cycles were required to compensate for changes and decaying sensitivity of the surface of the detector (Regener, 1964; Hodgeson, 1970).

Improvement was made in the stability of the surface response in a modification added by Bersis and Vassiliou (1966), in which gallic acid is also adsorbed on the surface in excess. The O_3 apparently reacts with and consumes the gallic acid rather than Rhodamine-B. An energy transfer step to Rhodamine-B subsequent to the initial reaction results in the same chemiluminescence from the dye compound, which is now no longer consumed. A commercial analyzer, Phillips Model PW9771, is based on this principle and has been designated as an equivalent method under EPA regulations.

5.5.4.2.3 Ultraviolet photometry. Ozone has a moderately strong absorption band in the ultraviolet (UV), with a maximum very near the mercury 254 nm

TABLE 5-7. PERFORMANCE SPECIFICATIONS FOR AUTOMATED METHODS

Performance parameter	Units	Specification
Range	ppm	0 to 0.5
Noise	ppm	0.005
Lower detectable limit	ppm	0.01
Interference equivalent		
Each interferant	ppm	±0.02
Total interferant	ppm	0.06
Zero drift, 12 and 24 hour	ppm	±0.02
Span drift, 24 hour		
20% of upper range limit	percent	±20.0
80% of upper range limit	percent	±5.0
Lag time	minutes	20
Rise time	minutes	15
Fall time	minutes	15
Precision		
20% of upper range limit	ppm	0.01
80% of upper range limit	ppm	0.01

Source: U.S. EPA, 40 CFR, Part 53.

emission line. This band is essentially a continuum near 250 nm. The molar absorption coefficient at the mercury line has been measured by several investigators with good agreement and has an accepted value of 134 M^{-1} cm^{-1} (base 10) at 0°C and 1 atm (Hampson et al., 1973). The UV absorption at 254 nm has long been used as a method of measuring gas-phase O_3 in fundamental chemical and physical studies. Some of the very first atmospheric O_3 measurements were, in fact, made by UV photometry; e.g., the Kruger Photometer. These early instruments and the problems with their use are described more completely in the first criteria document for photochemical oxidants (U.S. Department of Health, Education, and Welfare, 1970). The major problem with the older photometric instruments was the large imprecision involved in measuring the very small absorbance values obtained. For example, an absorbance value of 0.005 is a typical minimum for most conventional photometric measurements. At this

TABLE 5-8. LIST OF DESIGNATED REFERENCE AND EQUIVALENT METHODS

	Fed. Register notice			Designation
Identification and source	Vol.	Page	Date	(E=equivalent, R=reference)
Beckman Model 950A Ozone Analyzer Beckman Instruments 2500 Harbor Boulevard Fullerton, CA 92634	42	28571	6/3/77	R
Bendix Model 8002 Ozone Analyzer The Bendix Corporation Post Office Drawer 831 Lewisburg, WV 24901	41 45	5145 18474	2/4/76 3/21/80	R
Columbia Scientific Industries Model 2000 Ozone Meter 11950 Jollyville Road Austin, TX 78759	44	10429	2/20/79	R
Dasibi Model 1008-AH Ozone Analyzer	48	10126	3/10/83	E
Dasibi Model 1003-AH 1003-PC or 1003-RS Ozone Analyzers Dasibi Environmental Corp. 616 E. Colorado Street Glendale, CA 91205	42	28571	6/3/77	E
MEC Model 1100-1 Ozone Meter, MEC Model 1100-2 Ozone Meter, or MEC Model 1100-3 Ozone Meter Columbia Scientific Industries 11950 Jollyville Road P.O. Box 9908 Austin, TX 78766	41 42	46647 30235	10/22/76 6/13/77	R
Meloy Model OA 325-2R Ozone Analyzer	40	54856	11/26/75	R
Meloy Model OA 350-2R Ozone Analyzer Columbia Scientific Industries 11950 Jollyville Road Austin, TX 78759	40	54856	11/26/75	R
Monitor Labs Model 8810 Photometric Ozone Analyzer Monitor Labs, Incorporated 10180 Scripps Ranch Boulevard San Diego, CA 92131	46	52224	10/26/81	E

TABLE 5-8. LIST OF DESIGNATED REFERENCE AND EQUIVALENT METHODS (continued)

Identification and source	Fed. Register notice Vol.	Page	Date	Designation (E=equivalent, R=reference)
Monitor Labs Model 8410E Ozone Analyzer Monitor Labs, Incorporated 4002 Sorrento Valley Boulevard San Diego, CA 92121	41	53684	12/8/76	R
PCI Ozone Corporation Model LC-12 Ozone Analyzer PCI Ozone Corporation One Fairfield Crescent West Caldwell, NJ 07006	47	13572	3/31/82	E
Philips PW9771 O_3 Analyzer Philips Electronic Instruments, Incorporated 85 McKee Drive Mahwah, NJ 07430	42 42	38931 57156	8/1/77 11/1/77	E
Thermo Electron Model 49 UV Photometric Ambient O_3 Analyzer Thermo Electron Corporation Environmental Instruments Division 108 South Street Hopkinton, MA 01748	45	57168	8/27/80	E

value, a photometer pathlength of almost 1 km would be required to measure a concentration of 0.01 ppm, the minimum value specified for acceptable automated methods (Table 5-7).

This problem of adequate sensitivity with moderate pathlengths has been overcome by modern digital techniques for measuring small absorbancies. The first instrument of this new generation of photometers was marketed by Dasibi of Glendale, California, in the early 1970s. The details of this instrument have been described by Bowman and Horak (1972). Several other commercial instruments have since been marketed and, along with the Dasibi, have been designated as equivalent methods by EPA (Table 5-8). All of these instruments operate effectively as double-beam digital photometers. A transmission signal is averaged over a finite period of time with O_3 present and is compared to a similar transmission signal obtained through an otherwise identical reference air stream from which the O_3 has been preferentially scrubbed. The electronic comparison of the two signals can be converted directly into a digital display of O_3 concentration. In the Dasibi instrument, the O_3 is removed during the reference cycle by a manganese dioxide scrubber, through which other species that absorb at 254 nm should pass unaffected.

The UV photometric technique has the advantages, like gas-solid chemiluminescence, that a reagent gas flow is not required and that sample air flow control is not critical. In addition, the measurement is in principle an absolute one, in that the concentration can be computed directly from the measured absorbance since the absorption coefficient and the pathlength are known. This capability is used extensively for the purpose of O_3 calibration as discussed in section 5.5.5. Commercial UV photometers for O_3 can serve a dual function as a secondary standard for O_3 calibration, if they are in turn calibrated against a primary UV standard such as those provided by the National Bureau of Standards (NBS) (Bass et al., 1977). In practice, UV photometric analyzers that are used for monitoring O_3 concentrations in the atmosphere are calibrated with standard O_3 samples in order to compensate for possible O_3 losses in the sampling and inlet systems. A UV photometric analyzer has the potential disadvantage that any molecular species that absorbs at 254 nm (e.g., SO_2, benzene, mercury vapor) and that may also be removed along with O_3 during the reference cycle can interfere. Documentation of such interference during atmospheric monitoring is lacking at present.

5.5.5 Generation and Calibration Methods for Ozone

Unlike the other criteria pollutants, O_3 is a thermally unstable species that must be generated *in situ* during the calibration of analyzers used for atmospheric monitoring. This creates special requirements not encountered with other pollutants and thus this section deals with means for generating dynamic air streams containing stable O_3 concentrations and chemical and physical means for absolute measurement of these concentrations.

5.5.5.1 Generation. Ozonized samples of air can be produced by a number of means, including photolysis (Brown and Milford, 1960), electrical discharge (Toyami and Kobayashi, 1966), and radiochemical methods (Steinberg and Dietz, 1969). Electrical discharges are useful for producing high concentrations of O_3 in air for other applications; e.g., O_3 chemistry. Radiochemical methods would be ideal except for their cost and required safety features. By far the most common method, however, for generating low concentrations of O_3 in air involves the photolysis of molecular oxygen.

$$O_2 + h\gamma(\lambda<200 \text{ nm}) = 2O \tag{5-68}$$

$$O + O_2 + M\ (M = N_2 \text{ or } O_2) = O_3 + M \tag{5-69}$$

One of the most common photolytic generators uses a mercury vapor 6- or 8-inch PenRay photolysis lamp positioned parallel to a quartz tube through which a controlled rate of air flows. The O_3 concentration is simply varied by means of an adjustable and calibrated mechanical sleeve placed over the lamp envelope (Hodgeson et al., 1972b) or by varying the voltage or current supplied to the lamp.

5.5.5.2 Calibration

5.5.5.2.1 KI procedures: original EPA reference method. The output of photolytic O_3 generators can provide air samples containing stable O_3 concentrations over a considerable period of time with careful control of flow rate, lamp voltage, temperature, and pressure. It is necessary to calibrate these generators periodically with an absolute reference method. Prior to 1975, there were as many as seven different calibration methods for O_3 employed to varying extents in this country (National Academy of Sciences, 1977). A good part of the variability in older data may result from biases in calibration procedures. In an attempt to standardize the methodology, EPA published a reference calibration procedure with the reference method in 1971 when the oxidant (as O_3) standards were promulgated (U.S. Environmental Protection Agency, 1971a). This method was the 1 percent neutral buffered potassium iodide (NBKI) procedure, a technique that had been used by EPA and other agencies for some time.

During the early 1970s, it became evident that there were serious deficiencies with the NBKI reference method. Several problems with the NBKI procedure, summarized by a joint EPA-NBS workshop in 1974 (Clements, 1975), included the gradual continued release of iodine after sampling, variable results obtained with different types of impingers, reagent impurities, and a positive bias when compared to other O_3 measurement methods. In 1973, a significant bias was observed between calibration results obtained with the 1 percent unbuffered KI method used by the Los Angeles Air Pollution Control District (LAAPCD) and the 2 percent NBKI procedure used by the California Air Resources

Board (CARB). (The latter technique is very similar to the original 1 percent NBKI EPA reference method). As a result, an interagency collaborative study was undertaken to intercompare the LAAPCD, CARB, and EPA methods, using UV photometric O_3 measurements as the reference. The results of this study (Demore et al., 1976) demonstrated the positive bias of the NBKI methods. The results obtained by the EPA and CARB NBKI methods were higher by 15 to 25 percent than those obtained by UV photometry; whereas the results obtained with the unbuffered KI method were 4 percent lower and showed considerable scatter. Concurrent with and after these earlier reports, a large number of individual studies ensued on the evaluation of KI methods and their intercomparison with UV photometric O_3 measurements and O_3 measurements by gas-phase titration (GPT) with standard nitric oxide (NO) samples. The history of these studies will not be reviewed here since they were presented in the previous criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1978) and have been reviewed by Burton et al. (1976). The major conclusions from these studies are presented below.

1. Results obtained by NBKI procedures are higher than those obtained by UV photometry or gas-phase titration by 5 to 25 percent, depending on details of the procedure.
2. When O_3 is measured in the presence of humidified air, NBKI results tend to be even higher by another 5 to 10 percent (e.g., California Air Resources Board, 1975). The reason for this apparent moisture effect is not known.
3. In general, NBKI techniques are subject to large imprecision because of procedural variation.

Because of these difficulties, EPA published a notice in the October 6, 1976, Federal Register of its intent to evaluate alternative calibration procedures and to replace the NBKI procedure with one of four alternative procedures (U.S. Environmental Protection Agency, 1976). These four alternate procedures were based on (1) UV photometry, (2) GPT with excess NO, (3) GPT with excess O_3, and (4) a KI technique that uses boric acid as buffer (BAKI). In subsequent studies (Rehme et al., 1981), UV photometry was considered to give superior results in terms of accuracy, precision, and simplicity of use; and in 1979 Appendix D of 40 CFR, Part 50, was amended to designate UV photometry as the calibration procedure for O_3 reference methods (U.S. Environmental Protection Agency, 1979).

Although NBKI methods are no longer used in this country for the purpose of calibration, there is a considerable data base available on health and welfare effects, as well as atmospheric chemistry and monitoring, that is based on these methods as standards. Therefore, it is important to consider how these data may be evaluated and compared to newer effects and aerometric data based on the new UV calibration standard. Since a systematic bias is known to exist between calibrations by KI methods and UV photometric methods, it should be possible, in principle, to apply correction factors to convert from a KI reference to a UV photometric reference. There are several problems inherent in attempting such corrections, however. A fairly wide range of variations has been reported in the literature on the comparison of KI and UV photometric measurements. In addition, some of the studies report a significant intercept in the linear correlation of KI and UV photometric data. For example, in the interagency collaborative study (Demore et al., 1976), the relation between EPA NBKI data and UV photometric data fit the following linear equation,

$$[O_3]_{EPA} = 1.24\ [O_3]_{UV} - 0.035 \qquad (5\text{-}70)$$

(Standard Error = ±0.013)

when the intercept is expressed in units of ppm. As a result, the ratio of KI/UV measurements varied from approximately 1.0 for the lowest concentration measured (0.1 ppm) to 1.20 for the highest concentration measured (0.8 ppm). It is inappropriate, however, to apply a general correction factor for the intercept because the presence and magnitude of such an intercept will be strictly dependent upon procedural variations during calibration; e.g., KI reagent purity (Clements, 1975; Beard et al., 1977).

It should be possible to apply a correction factor related to the slope of the equation, since the slope determines the absolute relation between simultaneous measurements in the absence of effects leading to non-zero intercepts. Even the magnitude of the slope, however, can depend to some extent on procedural variables. As discussed previously, the presence of moisture in the calibration air increases the magnitude of the bias and the slope. Fortunately, both the CARB and the LAAPCD procedures called for the consistent use of humidified air, whereas the EPA reference method prescribed the use of dry air. In addition, the elapsed time between sample collection and color measurement will also affect the magnitude of the slope because of the slow liberation of iodine after sampling (Clements, 1975; Beard et al., 1977; Hodgeson, 1976). Other unknown experimental factors may also influence the slope; e.g., impinger design (Clements, 1976; Beard et al., 1977).

In view of these difficulties, it is tempting to ignore the problem and simply state that it is impossible or without meaning to attempt to apply correction factors. Nevertheless, there are considerable effects and aerometric data bases available that should have a positive calibration bias compared to newer data based on the UV photometry standard. Therefore, an assessment has been made of the previous KI versus UV intercomparisons and recommendations are given in Table 5-9 for correction factors to apply to calibration data for conversion from UV to a KI reference or vice versa. It should be emphasized that these factors could validly be applied to correct for a calibration bias only and can not be applied for comparison of data where other effects are present; e.g., the comparison of oxidants versus O_3 data where the effects of oxidizing or reducing interferences must be considered. In this assessment, consideration was given only to those studies in which the KI procedure was compared directly to UV photometry. Several studies have compared KI measurements to GPT measurements, but there have been some differences observed in the intercomparison of GPT and UV measurements. The recommended value for data based on the CARB method assumes the use of humidified air. The value recommended for the EPA method assumes that dry air was used and that color measurement was made immediately after sample collection.

The uncertainties assigned reflect the fact that a range of values has been reported for the ratios in previous studies. No uncertainty value is reported for the LAAPCD method because only one intercomparison (Demore et al., 1976) has been reported and no correction should be attempted for this method. Finally, whenever any attempt is made to convert from one data base

TABLE 5-9. FACTORS FOR INTERCOMPARISON OF DATA CALIBRATED BY UV PHOTOMETRY VERSUS KI COLORIMETRY

Calibration method	Ratio, KI/UV
EPA, 1% NBKI	1.12 ± 0.05
CARB, 2% NBKI	1.20 ± 0.05
LAAPCD, 1% UKI	0.96[a]

[a] Correction for this method not recommended; only one intercomparison has been reported.

to another, these uncertainties must be added by conventional error propagation techniques to the uncertainty inherent with the original measurement.

5.5.5.2.2 Ultraviolet photometry method. A major reason UV photometry was designated as the calibration procedure was the excellent precision of the photometric measurement. In the collaborative study by Rehme et al. (1981), measurement with ten individual UV photometers gave only a 3.4 percent variability when compared to a reference measurement system. Other significant factors in the selection of UV photometry were the inherent simplicity of UV photometric measurements and the ready availability of commercial instruments that can also serve well as transfer standards between laboratory photometers and field O_3 analyzers. (See National Academy of Sciences, 1977, and McElroy, 1979, for a discussion of transfer standards.)

It was also presumed that UV photometry gives more accurate results, since the accuracy is determined primarily by the O_3 absorption coefficient, which is well known (Hampson et al., 1973; Demore and Patapoff, 1976). The lack of any significant bias between the ten UV photometers and the reference system in the collaborative study was to be expected since the reference system was itself calibrated against a standard photometer. Although there is little doubt that the accuracy of O_3 measurements has been significantly improved by conversion to the UV basis, some question still exists regarding the absolute relation between O_3 measurements by UV photometry and O_3 measurements by GPT measurements based on either an NBS standard reference material (SRM) nitric oxide (NO) gas cylinder or an NO_2 SRM permeation tube. These intercomparisons have been made by several investigators over the past 10 years and have been summarized by Burton et al. (1976) and Paur et al. (1979). The agreement between GPT and UV measurements was generally close to 1:1, although in some cases O_3 measurements by GPT have shown a small positive bias with respect to UV measurements. In the EPA collaborative study (Rehme et al., 1981), a number of independent GPT measurement systems were compared to the reference measurement system and gave O_3 data that had a mean positive bias of 7 percent with respect to the UV reference. Demore and Patapoff (1976) reported a 1:1 agreement between simultaneous measurements of O_3 by GPT and UV with a 5 percent uncertainty on the ratio of these measurements. In a recent detailed study conducted at the National Bureau of Standards (NBS) (Fried and Hodgeson, 1982), O_3 measurements made with an NBS standard photometer (Bass et al., 1977) were compared to GPT measurements of O_3 that were standardized against both NO cylinders (NBS SRM) and NO_2 permeation tubes (NBS SRM).

Since the measurement of flow rates is a critical GPT variable and has been considered as a major source of error in GPT measurements (Demore and Patapoff, 1976), NBS facilities were used for making absolute flow measurements by both gravimetric and volumetric means. The results of this study were that values of O_3 measured by GPT based on NO_2 or NO SRMs agreed to within less than 1 percent, but that values of O_3 measured by UV were lower by a small but significant 3 percent. For a consideration of possible error sources, reference is made to the original article by Fried and Hodgeson (1982). In summary, the UV photometric O_3 standard agrees quite closely with the NO and NO_2 measurement standards by GPT, as it should in principle. The resolution of any small biases that remain seems an appropriate matter for consideration by EPA and NBS.

The measurement principle for the absolute measurement of O_3 by UV photometry is the same as that used by instruments for monitoring atmospheric O_3 as described in section 5.5.4.2.3 (Bowman and Horak, 1972; Demore et al., 1976; Bass et al., 1977). Ozone is measured in a dynamic flow system by measuring the transmission, I/Io, of ozonized clean air in an absorption cell of pathlength, ℓ. When the concentration is to be expressed in units of ppm, measurement of temperature and pressure is also required. The O_3 concentration may then be calculated directly from the Beer-Lambert equation:

$$[O_3]_{ppm} = \frac{10^6}{\alpha l} \times \frac{T}{273} \times \frac{760}{P} \ln \frac{Io}{I} \qquad (5\text{-}71)$$

where α = O_3 absorption coefficient at 254 nm, 1 atm, and 0°C,
= 308 ± 4 $atm^{-1}cm^{-1}$ (log base e),

and

T = temperature, °K;
P = pressure, torr.

Laboratory photometers used for primary O_3 calibrations have pathlengths of 1 to 5 meters and sophisticated digital electronic means for measuring small absorbancies (Bass et al., 1977; Bowman and Horak, 1972).

A major difference between a photometer for calibration and one for atmospheric monitoring is that the calibrator uses clean air during the reference cycle rather than chemically scrubbed ambient air. The conversion of a commercial O_3 photometric monitor to a photometer for use as a transfer standard for calibration has been described by Paur and McElroy (1979). Definitions are in order here. A primary standard UV photometer is one that meets the requirements and specifications given in the 1979 revision of the O_3 measurement and calibration procedures (U.S. Environmental Protection Agency, 1979). A transfer standard as used by EPA is a device or a method that can be calibrated against a primary photometer and transferred to another location for calibration of O_3 analyzers. Commercial O_3 photometers have served well in this regard, but other devices have been used as well; e.g., calibrated generators and GPT apparatus. Guidelines on transfer standards for O_3 have been published by EPA (McElroy, 1979), and reference has already been made to the NAS discussion on transfer standards (National Academy of Sciences, 1977). Recently a laboratory photometer has been developed by Paur and Bass (1983) for use in the quality assurance program at EPA on O_3 measurements. Some unique features of this instrument include the mechanism for making the absorbance measurement; internal temperature and pressure transducers; and a minicomputer for controlling the measurement cycle, computing O_3 concentrations, and labeling, storing, and printing calibration data.

The use of UV photometry is unique in air pollution measurements in that it is based on a physical measurement principle rather than a chemical standard. It is then worthwhile to trace how the measurement chain works from a primary standard to field measurements. The primary standard is referenced to the accepted O_3 absorption coefficient. Transfer standards are then calibrated with primary photometers maintained at EPA, NBS, and elsewhere. The use of commercial photometers in this regard has been described by several investigators (Demore et al., 1976; Hodgeson et al., 1977). These and other kinds of transfer standards are then used to calibrate O_3 analyzers used for field measurements.

5.5.5.2.3 Other procedures. Although UV photometry has been specified as the reference calibration procedure, other procedures are available that can give equivalent results. These include the BAKI method, which was allowed as an interim alternative method for the calibration of O_3 monitors when the UV method was designated in 1979. Other KI methods that have been used successfully in Europe are also briefly discussed here. Finally, the GPT method is reviewed since it has been used extensively in this country and was discussed above with regard to the cross-check of method accuracies.

In the California collaborative study already cited (Demore et al., 1976), the 1 percent unbuffered KI (UKI) procedure showed no significant bias compared to the reference UV procedure. Because it used a titration procedure for measuring the iodine produced, the technique suffered from large imprecision and its application was not pursued. Thus, the key reason that the method was not biased was apparently overlooked at the time; that is, the method did not employ the phosphate buffer. A major problem with NBKI techniques is the slow release of iodine and continued color development after sampling. Flamm (1977) evaluated the rate of this iodine production and found that it was the same as the rate with which hydrogen peroxide (H_2O_2) releases iodine from the same solution. Based on this observation and a consideration of other possible species that might be responsible, Flamm concluded that certain buffer anions, including phosphate, catalyze the formation of H_2O_2 and yield stoichiometries for iodine production greater than 1. Measurements made with a 1 percent KI reagent containing 0.1 M boric acid (BAKI), pH=5, did not exhibit this phenomenon and gave answers that agreed closely with measurements by UV photometry. These results have been confirmed in other studies (Hodgeson, 1976; Rehme et al., 1981).

The BAKI method was evaluated as one of four alternative techniques in the collaborative study conducted by EPA (Rehme et al., 1981). No significant bias was observed between BAKI and the reference technique based on UV photometry. An analysis, however, of BAKI measurements by ten volunteers revealed a large system-dependent variability, and thus the BAKI technique was not recommended as an independent calibration method. It is noteworthy that the system variability attributable to calibration was reduced somewhat if each operator assumed a molar absorption coefficient for iodine (as I_2) of 25,600 $M^{-1}cm^{-1}$ rather than independently measuring the absorption coefficient with standard I_2 solutions as these procedures usually prescribe. The BAKI technique was allowed by EPA as an alternative procedure for the calibration of O_3 monitors, but only for a period of 18 months following the 1979 amendment. Measurement systems based on the BAKI procedure may still be certified as transfer standards provided the guidelines for certification given in the EPA technical assistance document for such standards are followed (McElroy, 1979).

Methods based on iodometry have been used in Europe for some time for the calibration of O_3 analyzers. Bergshoeff (1970) described a method for use in the Netherlands, in which thiosulfate is added to the KI reagent (KIT method) along with 0.1 M phosphate buffer. The iodine released is immediately reduced by the thiosulfate and the amount of iodine consumed is determined by back-titration of the thiosulfate. This method has the advantage that problems associated with iodine instability in solution are eliminated. In the Federal Republic of Germany, the standard is based on a 2 percent KI reagent with 2 percent KBr (KIBr Method) and a low concentration (0.02 to 0.03 M) of phosphate buffer (Van de Wiel et al., 1978). These techniques have been compared to UV and GPT measurement procedures by Van de Wiel et al. (1978). Measurements made with the KIBr method were in essential agreement with measurements by UV or GPT, while measurements by the KIT method were too high by 15 to 25 percent, depending on the relative humidity of the samples. Modifications have since been made in the KIT method by the addition of KBr and reduction of the phosphate concentration.

The gas-phase titration (GPT) method employs the moderately rapid bimolecular reaction between O_3 and NO to produce NO_2 (Rehme et al., 1974):

$$NO + O_3 = NO_2 + O_2 \qquad (5\text{-}72)$$

This approach was, in fact, one of the early methods used to measure the absorption coefficient of O_3 (Clyne and Coxon, 1968) and yielded excellent agreement with other absolute techniques (Demore and Patapoff, 1976). When NO is present in excess, no side reactions occur and the stoichiometry is as given above. This method has the distinct advantage that it gives an absolute relation among three common pollutants. A measurement of the quantity of NO or O_3 consumed or NO_2 produced provides a simultaneous measurement of the other two species and the GPT procedure has been used in all three modes. This calibration technique is often used in the calibration of chemiluminescence NO_x ($NO + NO_2$) analyzers. In order to obtain accurate concentration measurements in the procedure as normally employed, accurate flow measurements are required; and this is the principal complexity and difficulty with this procedure (Demore and Patapoff, 1976). Because of this problem and unexplained biases between GPT measurement systems and the UV reference in the EPA collaborative study, the GPT method was not recommended as an independent calibration technique (Rehme et al., 1981). It is still allowed, however, as a transfer standard in accordance with the EPA guidelines for these standards (McElroy, 1979).

5.5.6 Relationship between Methods for Total Oxidants and Ozone

When the ambient air quality standards for criteria pollutants were originally established, a numerical standard was set for photochemical oxidants as defined by measurements based on iodometric techniques. Much of the health-related and welfare-related evidence used as the basis for the standards was obtained using the total oxidant instrumentation discussed above. The reference method specified in 1971, however, was the chemiluminescence measurement of O_3. Although not specifically stated at the time, the reasons for specifying O_3 measurements were undoubtedly the following. First, instrumental methods for the specific measurement of atmospheric O_3 became commercially available in 1970. These had several very practical advantages over total oxidant KI-based instruments. These advantages were greater sensitivity, precision, specificity--no interferences from ambient SO_2 and NO_2--and improved reliability in routine monitoring. Second, the data available showed that O_3 was the major contributor to total oxidant measurements, that O_3 was the major contributor to observed health and welfare effects, and that O_3 could probably serve, then, as the best surrogate for measurements of total oxidants and for controlling effects of oxidants in ambient air (see reviews in Burton et al., 1976; U.S. Environmental Protection Agency, 1978).

Notwithstanding the promulgation of standards for ozone rather than photochemical oxidants by EPA in 1979, an examination of the temporal and quantitative relationships between total oxidant and O_3 data remains of considerable interest, largely because pre-existing data and many newer data on health and welfare effects were obtained by means of total oxidant methods. Aside from the relative paucity of data on simultaneous measurements, there are two distinct problems in making such comparisons. The first is the difficulty in estimating the contributions to the total oxidant measurements from other oxidizing species such as NO_2 and from reducing species such as SO_2. The presence of such species could cause the total oxidant measurements to be either higher or lower than O_3 concentrations. The second difficulty is in estimating the bias created between past and present data as a result of the change from the NBKI to the UV photometry calibration procedures. Fortunately, these two problems can be treated separately and the latter problem vanishes for comparison of simultaneous O_3 and oxidant data obtained using the same calibration procedure.

In the sections below, the relationship that should exist between total oxidant and O_3 is considered from an evaluation of the response of NBKI measurements to other oxidizing and reducing species. The predicted relationship is then compared to data obtained in simultaneous field measurements of total oxidant and O_3.

5.5.6.1 Predicted Relationship. The predicted total oxidant measurements can be expressed as the sum of the contributions from oxidizing and reducing species that release or consume iodine in NBKI reagent:

$$\begin{aligned}[\text{Total Ox}] = {} & a[O_3] + \Sigma_i\ b_i\ [\text{Ox}]_i + c[NO_2] \\ & d[SO_2] - \Sigma_i\ e_i\ [\text{Red}]_i\end{aligned} \qquad (5\text{-}73)$$

In this equation, $[\text{Ox}]_i$ and $[\text{Red}]_i$ represent the concentrations of other oxidizing and reducing species in the atmosphere. The atmospheric concentrations of other reducing species, such as H_2S, are normally quite low compared to SO_2 concentrations (Stevens et al., 1972b, and references therein) and these species will not be considered further here. If the concentrations above are true atmospheric concentrations, the constants a, b, c, and d represent the efficiencies with which the various species release or consume iodine. For example, the value of the constant, a, for an oxidant instrument calibrated by the CARB 2 percent NBKI method would be approximately 1.2 (section 5.5.5.2). Since the instruments are calibrated with ozonized air, the factor, a, represents the bias of the calibration method used. If the O_3 concentration is overestimated because of calibration bias, then so are the contributions of the other species by the same factor; i.e., the constants b, c, and d are all higher than their true values by the same constant, a. Therefore, it should in principle be possible to correct total oxidant data for calibration bias by dividing both sides of the equation above by a.

$$\begin{aligned}[\text{Total Ox}]' &= [\text{Total Ox}]/a \\ &= [O_3] + \Sigma_i\ b'_i\ [\text{Ox}]_i\ c'[NO_2] + d'[SO_2]\end{aligned} \qquad (5\text{-}74)$$

As discussed previously (section 5.5.5.2), whenever such a correction is attempted, the net uncertainty in the total oxidant data will have to be increased by an amount equivalent to the uncertainty in the calibration bias factor. Next, literature values reported for b_i, c, and d will be discussed.

The magnitude of these factors, together with estimated atmospheric concentrations, will be used to compare predicted relationships between total oxidants and O_3.

Other atmospheric oxidants that have been identified and that may contribute to the total oxidant reading are hydrogen peroxide (H_2O_2), small organic peroxides (e.g., methyl and ethyl hydroperoxide), peracetic acid, peroxyacyl nitrates (Cohen et al., 1967b), and pernitric acid (Niki et al., 1976). An estimation of the contribution of these species to the total oxidant measurement is quite difficult because individual b_i's have not been measured and there are few data available on atmospheric concentrations of individual species. The magnitude of the efficiency term will depend not only on the stoichiometry of the oxidation reaction, but also on the rate. For many of the oxidants above, the overall stoichiometry may be equivalent to that of O_3, given sufficient time for completion of the reaction. Cohen et al. (1967b) reported nearly equal molar absorption coefficients for iodine production by O_3, H_2O_2, peracetic acid, acetyl peroxide, and ethyl hydroperoxide. Only O_3 and peracetic acid gave immediate color development and the others were classified as slow oxidants because the color developed slowly. A summary of the effects of various oxidants on NBKI reagent and the Mast oxidant meter is given in Table 5-10 (Cohen et al., 1967b; Purcell and Cohen, 1967; Burton et al., 1976).

In contrast to the b_i terms, reaction efficiencies for NO_2 and SO_2 are relatively well known. The most definitive study of the effect of NO_2 is by Tokiwa et al. (1972). In that study the reaction efficiencies were 6 percent for the Mast oxidant meter, 22 percent for a 10 percent KI colorimetric analyzer, and 32 percent for a 20 percent KI colorimetric analyzer. At the 20 percent KI concentration, the reaction efficiency actually varied from 33 percent at zero O_3 concentration to 19 percent at an O_3 concentration of 0.6 ppm. Some of the earlier studies reported a negative interference from SO_2 but gave variable values for the magnitude of the effect (Cholak et al., 1956; Deutsch, 1968). It is now well-documented that SO_2 is a quantitative negative interference with a 100 percent efficiency for reducing the oxidant reading by an amount equivalent to the SO_2 concentration present (Cherniack and Bryan, 1965; Saltzman and Wartburg, 1965).

Returning to the analytical expression for total oxidant, an "adjusted" or corrected oxidant value can be expressed as below, assuming that the same

TABLE 5-10. RESPONSE OF NBKI REAGENT AND MAST METER TO VARIOUS OXIDANTS[a]

	NBKI	Mast
Ozone	A[a]	E
Peracetic acid	A	-
Hydrogen peroxide	B	D
Acetyl peroxide	B	N
Ethyl hydroperoxide	B	-
n-Butyl hydroperoxide	B	-
tert-Butyl hydroperoxide	B	-
Nitrogen oxides (NO_x)	D (10% as NO_2)	D (10%)
Peroxyacetyl nitrate (PAN)	D	N
Peroxypropionyl nitrate (PPN)	D	D

[a] A = immediate color development; B = slow color development; D = positive interference; E = good response; and N = no response (or negligible).

Source: Cohen et al. (1967).

calibration procedure is used for total oxidant and O_3, and assuming that no other significant reducing interferences are present:

$$\begin{aligned}[\text{Total Ox}]_{\text{corr.}} &= [\text{Total Ox}] - c[NO_2] + [SO_2] \\ &= [O_3] + \Sigma_i\, b_i\, [\text{Ox}]_i\end{aligned} \tag{5-75}$$

Thus, a total oxidant measurement for which legitimate corrections or compensations for NO_2 and SO_2 have been made should always be higher than a simultaneous O_3 measurement by an amount that is a function of the type and concentrations of other oxidants present. The only major qualifications to this prediction are that both types of measurements must be sampling the same air mass and be calibrated with respect to the same reference; that no other significant reducing interferences are present; and that O_3 losses within the sample inlet system are insignificant. On the other hand, total oxidant data uncorrected for SO_2 and NO_2 interferences may be higher or lower than corresponding O_3 data, depending on the concentrations of these pollutants. Because of the potential presence of these interferences, it is quite difficult or impractical to compare oxidant and O_3 measurements during evening and early morning hours, when O_3 concentrations are quite low. As shown in chapter 2 and discussed in chapter 4, however, when the O_3 concentration has reached its diurnal maximum value during late morning or early afternoon hours, the NO_2 concentration is near a minimum and is low compared to the O_3 concentration (Leighton, 1961; Stevens et al., 1972a). Likewise, at the O_3 maximum, the SO_2 concentration also is often, but not always, small compared to the O_3 concentration, particularly in studies done in California (Dickinson, 1961; Ballard et al., 1971a; Stevens et al., 1972b). Therefore, in the comparison of total oxidant and O_3 simultaneous field measurements below, emphasis is placed on comparison of peak hourly averages. This seems especially appropriate since the oxidant standard and compliance monitoring are based on the second-highest hourly average (U.S. Environmental Protection Agency, 1979).

5.5.6.2 Empirical Relationship Determined from Simultaneous Measurements. Because of the difficulties and uncertainties in predicting the relationship between O_3 and oxidant measurements, this comparison is best determined by simultaneous measurements of the atmosphere. Nevertheless, the predicted relation discussed above is useful in evaluating results from field measurements. Several precautions should be taken in performing simultaneous measurements. Both kinds of instruments must be calibrated frequently with the same ozonized air stream that has been analyzed by a common reference method. In a simultaneous comparison, daily calibrations should be made with an O_3 generator and the generator output should be analyzed weekly. Both instruments should sample the same air parcel. Routine maintenance should be frequent to ensure constant gas and reagent flow rates, clean sample inlet systems, etc. Finally, in any meaningful comparison of O_3 and oxidant data, simultaneous measurements of NO_2 and SO_2 should be made. If chromium trioxide scrubbers are used to remove SO_2 in the inlet to the oxidant instrument, these must be frequently tested to ensure that O_3 is not also removed during continued use, particularly under very humid conditions. These scrubbers may cause some additional bias by oxidation of NO to NO_2. During stagnation periods in cities, NO can build up to high concentrations in the morning and oxidation of NO by the scrubber will give a significant response in colorimetric analyzers. Several studies on the comparison of total oxidant and O_3 measurements have been made and are summarized below. In some cases the precautions noted above were taken and in some cases they were not.

The earliest comparative study reported was by Renzetti and Romanovsky (1956). This study compared a phenolphthalein total oxidant monitor, a KI continuous oxidant monitor, a rubber-cracking apparatus, and an open-path ultraviolet spectrometer, which monitored the UV absorption at characteristic O_3 absorption wavelengths. The only meaningful measurements for consideration here are the KI oxidant and UV O_3 measurements, since these are similar to measurement methods used later. The KI oxidant monitor was the version (Littman and Benoliel, 1953) used for later colorimetric oxidants measurements, but used with a 20 percent KI rather than 10 percent KI reagent. The UV O_3 spectrometer, however, differed in a number of respects from the O_3 photometers in use today. Measurements were made across an open optical path of 325 ft of the transmission at three wavelengths, λ_1 = 265 nm, λ_2 = 313 nm, and λ_3 = 280 nm. Intensity ratios at the three wavelengths were used to minimize the effects of other UV absorbers and of particulate scattering. Some non-O_3 absorption may still have been present, and, if so, the measured values would be higher than the true O_3 values. The published absorption coefficients at these three wavelengths were used to compute O_3 concentrations (Vigroux, 1952). This should not be a serious source of inaccuracy since laboratory measurements of these coefficients have not changed significantly (Demore et al., 1976). Measurements were made over a 4-month period. Figures 5-3 and 5-4 are illustrative of the data obtained for a single day or a monthly average. Peaks of total oxidant and of O_3 occurred at the same time, but the O_3 maximum was usually less than the total oxidant maximum. The UV O_3 data were usually higher in the wings at low O_3 concentrations. If this effect was the result of particulate scattering or absorption by other UV absorbers, which is possible, these same interferences were likely to have been present at the peak O_3 concentration also, and the concentration was then overestimated. Renzetti and Romanovsky attributed the higher total oxidant reading to the presence of "other oxidants" and estimated concentrations of other oxidants of 0.1 to 0.4 ppm, depending on O_3 concentration. Since the total oxidant instrument was calibrated by an NBKI method, this estimate is almost certainly too high and a large portion of the difference between oxidant and O_3 may have been a result of the 20 to 25 percent positive calibration bias. Since interferences may be present in the UV measurement and simultaneous measurements of NO_2 and SO_2

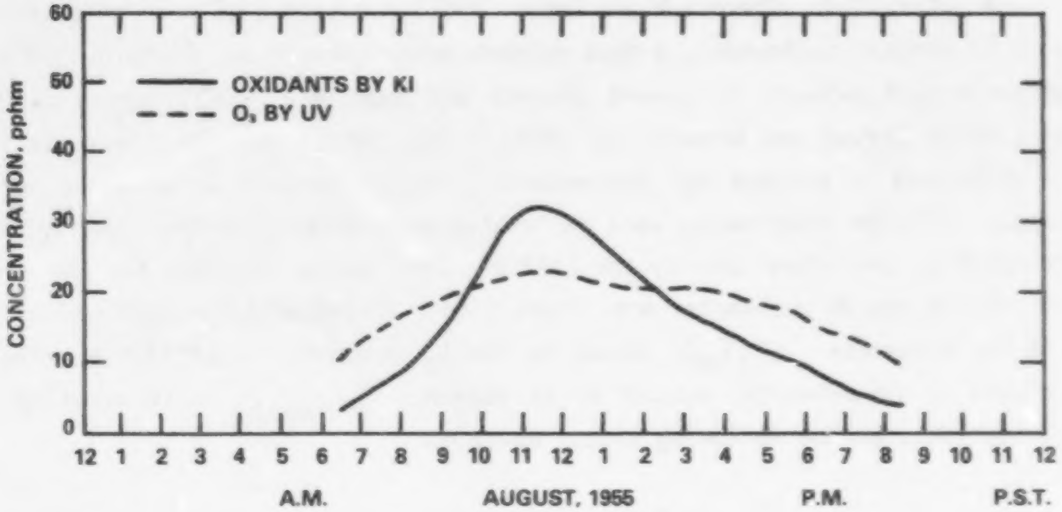


Figure 5-3. Ozone and oxidant concentration in the Pasadena area, August 1955.

Source: Renzetti and Romanovsky (1956).

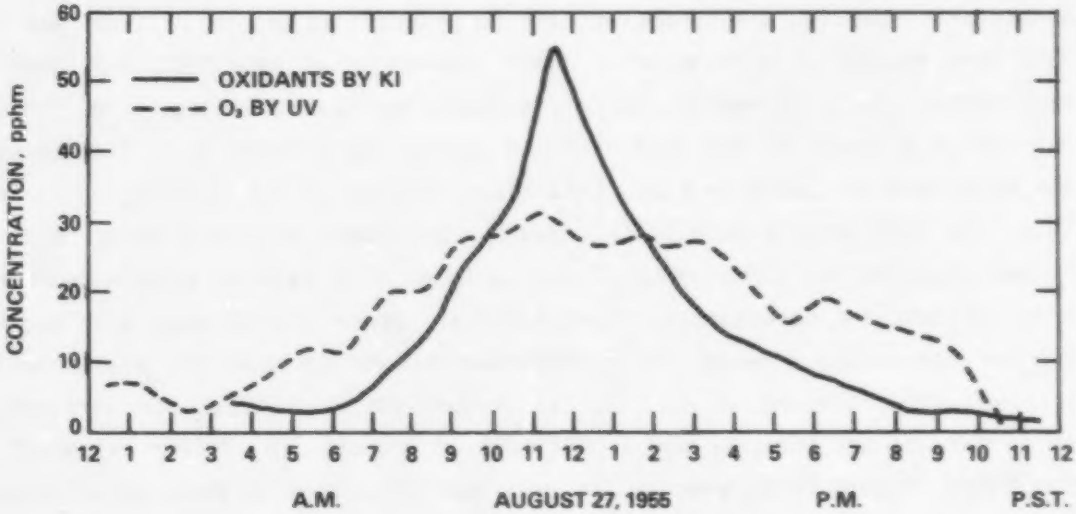


Figure 5-4. Ozone and oxidant concentration in the Los Angeles area.

Source: Renzetti and Romanovsky (1956).

were not available at the time, no attempt is made to make any more quantitative assessment of this study.

A later study (Cherniack and Bryan, 1965) compared a 10 percent colorimetric KI oxidant instrument, a Mast oxidant meter (Brewer and Milford, 1960), a galvanic-cell oxidant instrument (Hersch and Deuringer, 1963), and a UV O_3 photometer (Bryan and Romanovsky, 1956). This latter instrument was similar in principle to present-day photometers. The precautions noted above were taken. All the instruments were calibrated with respect to the 2 percent UKI calibration procedure used by the LAAPCD. The results obtained for the calibration of the UV photometer are interesting. The absolute concentrations for the UV photometer ($[O_3]_{UV}$), based on the O_3 absorption coefficient, were related to colorimetric oxidant meter readings ($[O_3]_{OXID}$), calibrated by 2 percent UKI, by the following linear equation:

$$[O_3]_{UV} = 1.027\ [O_3]_{OXID} + 0.005 \qquad (5\text{-}76)$$

The corresponding slope in the later study by Demore et al. (1976), comparing the LAAPCD calibration method with UV photometry, was 1.04. Simultaneous SO_2 and NO_2 measurements were made, but no corrections were made because the concentrations were reported to be quite small during the period of comparison. Atmospheric sampling was conducted over an unspecified period of time, and the data were expressed in terms of a linear regression of data from each instrument versus the colorimetric oxidant analyzer as the reference. The linear regression analysis of the data over the concentration range 0 to 0.6 ppm gave the relationships shown in Table 5-11 after correction for calibration factors. Thus, the data show a much better absolute agreement and correlation between O_3 measurements and colorimetric total oxidant than between electrochemical total oxidant and colorimetric total oxidant. Other studies have also shown a similar comparison between the electrochemical and colorimetric measurements (Tokiwa, 1972; Stevens et al., 1972a; Stevens et al., 1972b). In addition, these data do not indicate any significant contribution by "other oxidants" to the total oxidant measurement. The only qualifications to these observations are that corrections for NO_2 and SO_2 were not made, although they were reported as low. The data in Table 5-11 represent the total concentration range; it would have been informative to examine individual relationships at the oxidant maximum.

TABLE 5-11. COMPARISON OF CORRECTED INSTRUMENT READINGS TO COLORIMETRIC OXIDANT READINGS DURING ATMOSPHERIC SAMPLING[a]

Instrument	m	b	r
Mast meter	0.896	-0.013	0.868
Galvanic cell	0.776	+0.004	0.867
Ozone photometer	0.980	-0.005	0.982

(y = Instrument reading
= mx + b; x = colorimetric oxidant measurement; m = slope; b = intercept;
r = correlation coefficient)

[a] Source: Cherniack and Bryan (1965).

During the 1970s, several studies were conducted on the intercomparison of O_3 and total oxidant instrumentation. The Research Triangle Institute (RTI) of North Carolina, under contract to EPA, conducted extensive field studies on O_3 and total oxidant measurements in both Los Angeles and St. Louis (Ballard et al., 1971a; Ballard et al., 1971b; Stevens et al., 1972a; Stevens et al., 1972b). Measurements were made for O_3 by chemiluminescence and for total oxidant by a colorimetric KI analyzer and a Mast meter. Calibrations were carried out frequently with an O_3 generator calibrated by the 1 percent NBKI method. Data processors were used to collect and store all monitoring and calibration data. Simultaneous NO_2 and SO_2 measurements were also made and the oxidant data reported were corrected for these interferences. In another pertinent study (Clark et al., 1974), several instruments for the specific measurement of atmospheric O_3 were intercompared by monitoring in a rural environment. These instruments were a commercial UV photometer, three different commercial gas-phase chemiluminescence analyzers, and a gas-solid chemiluminescence analyzer. The instruments were all calibrated by a common reference procedure and hourly-averaged field measurements were collected over a 1-month period in August 1972 (Clark et al., 1974). Davis and Jensen (1976) reported intercomparisons of Mast meter total oxidant measurements and chemiluminescence O_3 measurements. The instruments were not calibrated by the same procedure in that study, however, nor were any corrections attempted for SO_2 and NO_2 interferences. Okita and Inugami (1971) reported an intercomparison of KI total oxidant measurements with chemiluminescence O_3 measurements in the urban atmosphere of Musashino, Japan. An intercomparison of total oxidant by KI and O_3 by chemiluminescence in irradiated auto exhaust was reported by Carroll et al. (1971). In another extensive field study conducted at an air monitoring station near the Houston ship channel, Severs and coworkers (Severs, 1975; Neal et al., 1976) examined the relationship between ozone and total oxidants for this area by making simultaneous measurements with a gas-phase chemiluminescence O_3 monitor and a Beckman colorimetric total oxidant analyzer. Primary calibrations of the instruments were performed periodically using the EPA 1 percent NBKI method. Hourly-averaged measurements were accumulated over a period from May 1972 through December 1973. No corrections were attempted for NO_2 or SO_2 interferences, but during the latter part of this study (August-December 1973) a chromium trioxide scrubber was placed in the inlet of the total oxidant analyzer.

All of these 1970 studies were reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1978). Only the major conclusions are repeated here. In general, the averaged data showed fairly good qualitative and quantitative agreement between the diurnal variations of total oxidants and O_3. The usual trend was a slightly higher value for the total oxidants measurement at the maximum, a not unexpected result in view of the discussion above. Comparisons of monthly-averaged data taken from studies in Los Angeles and St. Louis are shown in Figures 5-5 and 5-6 (Stevens et al., 1972a; 1972b). The total oxidant data shown in Figure 5-6 are uncorrected and show distinct morning and evening peaks resulting from NO_2 interference (see chapter 2 for diurnal patterns of NO_2). Examination of data taken from individual days shows considerably more variation among the methods, with total oxidant measurements both higher and lower than O_3 measurements. Intercomparisons of only UV photometric and chemiluminescence O_3 analyzers have not shown these large variations (Clark et al., 1974; Wendt, 1975). In all probability, these variations result from the large imprecision and interferences in total oxidant measurement.

Two of the studies above reported consistently lower total oxidant measurements. In one of these (Davis and Jensen, 1976), the reference KI method was used for calibrating the chemiluminescence analyzer while a factory calibration was used for the Mast meter. As pointed out above, other studies have found low oxidant readings for the Mast meter as compared to colorimetric analyzers (Cherniack and Bryan, 1965; Tokiwa et al., 1972; Stevens et al.,

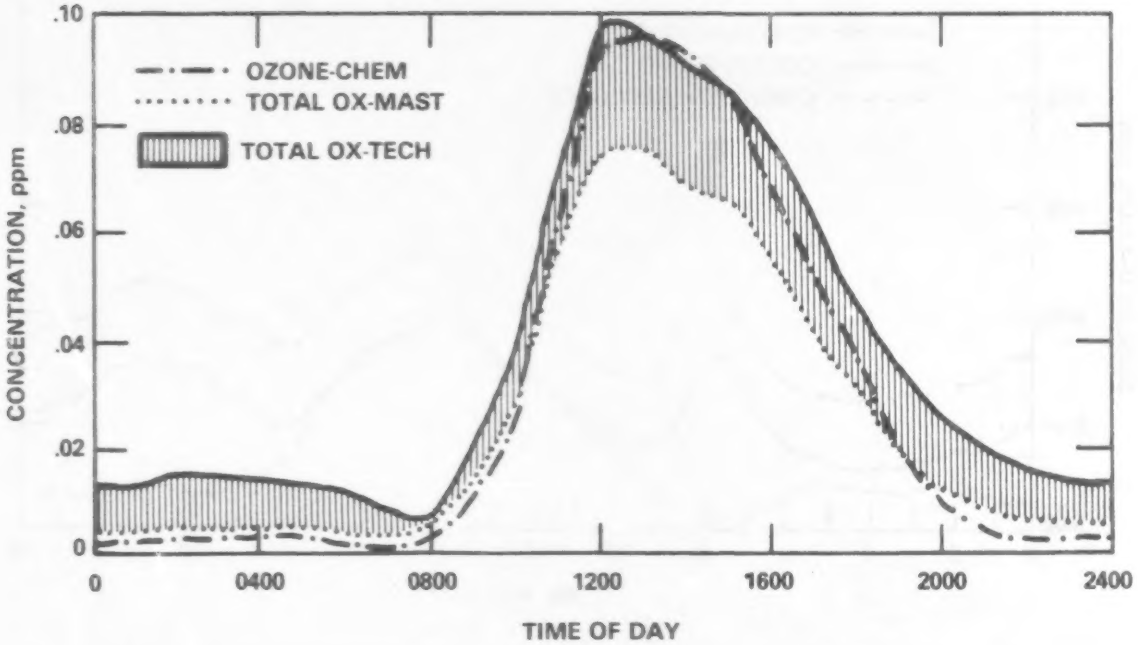


Figure 5-5. Measurements for ozone and oxidants in Los Angeles.

Source: Stevens et al., 1972b.

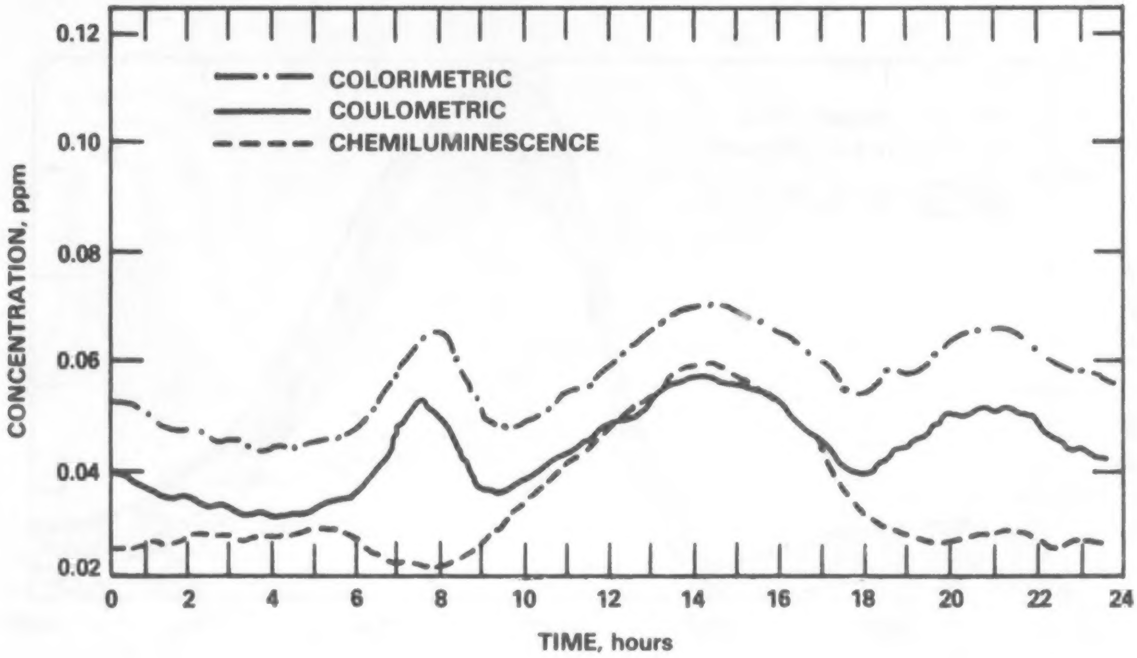


Figure 5-6. Measurements for ozone and oxidants in St. Louis.

Source: Stevens et al., 1972a.

1972a, 1972b). The use of the factory calibration would cause the Mast readings to be even lower because of a calibration bias (Cherniack and Bryan, 1965; Tokiwa et al., 1972). The results reported by Severs and coworkers are more difficult to evaluate. Chemiluminescence O_3 values generally higher, and sometimes considerably higher, than total oxidant measurements were reported, although the measurements were referenced to the same calibration procedure. Correlations were reported both with and without a chromium trioxide scrubber in the oxidant inlet. It is interesting that slightly better agreement was obtained without the chromium trioxide scrubber; but a large bias remained. These results are inconsistent with the known responses of the instruments and the results of other investigators, and it is probable that a serious measurement problem or interference existed in that study. The data reported for one day of high O_3, but abnormally low oxidants, are shown in Figure 5-7. It is highly improbable that the problem is with the chemiluminescence O_3 measurement, since this is typical of a normal O_3 diurnal variation and no other species are known to interfere. It is far more probable that some other species of pollutant in the highly industrialized area of the Houston ship channel repressed the response of the total oxidant analyzer, which thus does not respond to O_3, much less to any other oxidant.

The most recent comparison in the literature involved simultaneous O_3 and total oxidant measurements in the Los Angeles basin by the California Air Resources Board (1978) in the years 1974, 1976, and 1978. The maximum hourly data pairs were correlated (Chock et al., 1982) and yielded the following regression equation for 1978 data, in which a large number (927) of data pairs were available:

$$\text{Oxidant (ppm)} = 0.870\ O_3 + 0.005 \qquad (5\text{-}77)$$
$$\text{(correlation coefficient} = 0.92)$$

Thus, when the O_3 levels were relatively high, they were actually slightly higher than total oxidant. The total oxidant data were uncorrected for NO_2 and SO_2 interferences.

In summary, specific O_3 measurements agree fairly well with total oxidant corrected for NO_2 and SO_2 interferences and O_3 is the dominant contributor to total oxidant. Indeed, it is difficult to discern the presence of other oxidants in most total oxidant data. There can, however, be major temporal discrepancies between O_3 and oxidant data, which are primarily a result of

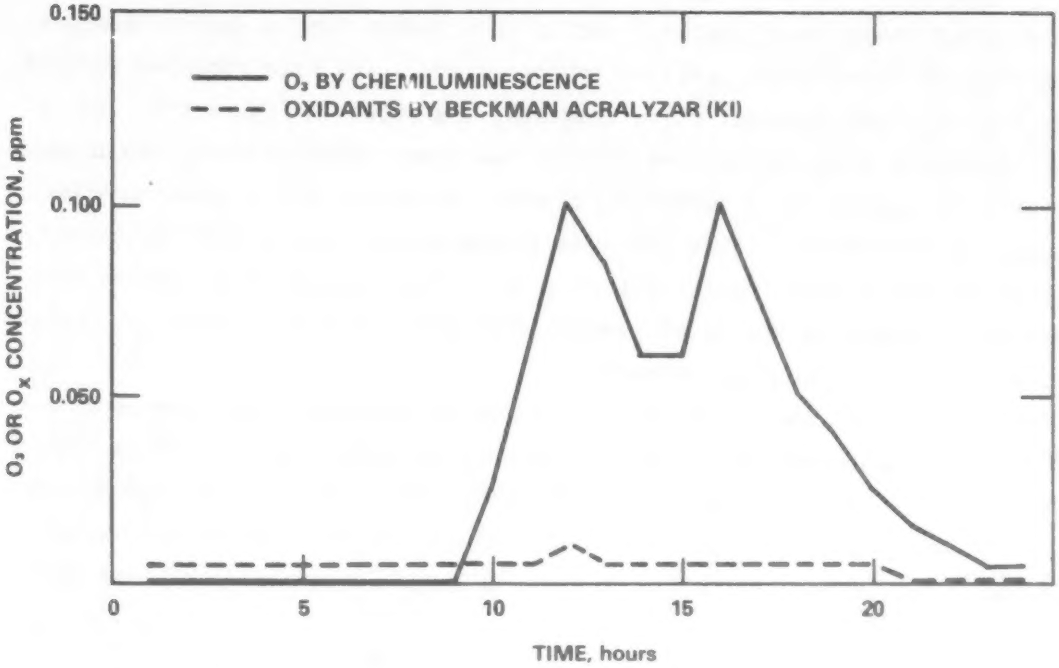


Figure 5-7. Measurement of ozone and oxidants, Houston Ship Channel, August 11, 1973.

Source: Severs (1975).

oxidizing and reducing interferences with KI measurements. As a result of these interferences, on any given day the total oxidant data may be higher than or lower than simultaneous O_3 data. The quantitative relationship between oxidant and O_3 data, such as that used by Chock et al. (1982), is probably quite location-dependent. From a methodologic standpoint, the measurement of O_3 is a more reliable indicator than total oxidant measurements of oxidant air quality; and such difficulties and controversy as may be involved in the intercomparison of O_3 and oxidant measurements are eliminated if the air quality standard is defined in terms of O_3.

5.5.7 Methods for Sampling and Analysis of Peroxyacetyl Nitrate and Its Homologues

5.5.7.1 Introduction. Since the discovery of the mysterious compound X (Stephens et al., 1956), later unambiguously identified as peroxyacetyl nitrate (PAN) (Stephens et al., 1961), much effort has been directed toward its atmospheric measurement. Peroxyacetyl nitrate is a product of photochemical reactions involving hydrocarbons and oxides of nitrogen (NO_x) in the atmosphere (Stephens, 1969). The significance of atmospheric PAN is twofold. It is a potent lachrymator and phytotoxicant in the ppb concentration range (Huess and Glasson, 1968). Because of the reversible thermal equilibrium (Hendry and Kenley, 1977),

$$CH_3O(O_2)NO_2 \rightleftarrows CH_3CO(O_2)\cdot + NO_2 \qquad (5\text{-}78)$$

which is sensitive to the NO_2/NO ratio, PAN may serve as an important reservoir for peroxy radicals and NO_2 (Singh and Salas, 1983a, 1983b) and may play a significant role in both the atmospheric nitrogen cycle and in tropospheric ozone formation (Spicer et al., 1983).

Only two analytical techniques have been used to obtain significant data on ambient PAN concentrations. These are gas chromatography with electron capture detection (GC-ECD) and long-path Fourier-transform infrared (FTIR) spectrometry. Atmospheric data on PAN concentrations have been obtained predominantly by GC-ECD because of its relative simplicity and superior sensitivity. These analytical techniques are described in section 5.5.7.2 along with attendant methods of sampling. Peroxyacetyl nitrate is somewhat analogous to O_3 in that it is a thermodynamically unstable oxidant and PAN standards must be generated and analyzed by some absolute technique for the purpose of calibrating the GC-ECD. Generation and calibration techniques are discussed separately in section 5.5.7.3. Finally, the analysis of PAN homologues is discussed briefly in section 5.5.7.4.

5.5.7.2 Analytical Methods. By far the most widely used technique for the quantitative determination of ppb concentrations of PAN is GC-ECD (Stephens, 1969). With Carbowax or SE30 as a stationary phase, PAN can be separated from components such as air, water, and other atmospheric compounds, as well as ethyl nitrate, methyl nitrate, and other contaminants that are present in PAN synthetic mixtures. Electron-capture detection (using a Nickel-63 source and a pulsed-current detector or a tritium source and a direct-current detector) provides sensitivity for PAN in the ppb and sub-ppb ranges. A typical column for the separation of PAN would be 3 to 5 feet in length and 1/8-inch in diameter (i.d.), and would be run isothermally at 25° to 60°C. Under these conditions, a peak assignable to PAN appears after 2 to 3 minutes. Table 5-12 shows parameters used by several investigators to determine trace levels of PAN by GC-ECD.

Sample injection into the GC is accomplished by means of a gas-sampling valve with a gas-sampling loop of a few milliliters volume (Stephens and Price, 1973). Sample injection may be performed manually or automatically. Typically, manual air samples are collected in 50 to 200 ml ungreased glass syringes, and purged through the gas-sampling valve. Samples collected from the atmosphere should be analyzed as soon as possible because PAN undergoes thermal decomposition in the gas phase and at the surface of containers. Automatic sample collection and injection may be accomplished by using a small pump to pull ambient air continuously through the sampling loop of an automatic sampling valve, which periodically injects the sample onto the column (Stephens and Price, 1973). Recently, Singh and Salas (1983b) have used cryogenic trapping of PAN, with liquid argon, from relatively large air samples for the purpose of measuring PAN concentrations in the sub-ppb range.

Most of the atmospheric PAN measurements have been made in polluted urban environments, where maximum concentrations of 5 to 50 ppb may occur, with average concentrations of a few ppb (Stephens, 1969; Lonneman et al., 1976). For the purpose of such measurements, chromatographic detection limits of 0.1 to 1 ppb are sufficient. The recent work of Singh and Salas (1983a, 1983b) on the measurement of PAN in the free (unpolluted) troposphere is illustrative of current capabilities for measuring low concentrations. A 50 to 200 ml volume

TABLE 5-12. SUMMARY OF PARAMETERS USED IN DETERMINATION OF PAN BY GC-ECD

Reference	Column dimensions and materials	Stationary phase	Solid support	Column temperature, °C	Flow rate, (ml/min)	Carrier gas	Elution time, min	Concentration range
Heuss and Glasson, 1968	4 ft x 1/8 in Glass	SE30 (3.8%)	80-100 Mesh Diatoporte S	25	N.A.	N.A.	N.A.	ppb range
Grosjean, 1983	6 ft x 1/8 in Teflon	10% Carbowax 400	60/80 Mesh Chromosorb P	30	40	N_2	N.A.	ppb range
Darley et al., 1963	3 ft x 1/9 in Glass	5% Carbowax 400	100-200 Mesh Chromosorb W	35	25	N_2	2.17	3 to 5 ppb
Stephens and Price, 1973	1.5 ft x 1/8 in Teflon	5% Carbowax E 400	Chromosorb G 80/100 Mesh treated with dimethyl dichlorosilane	25	60	N_2	1.75	37 ppb
Lonneman et al., 1976	3 to 4 ft x 1/8 in Glass	10% Carbowax 600	Gas Chrom Z	25	70	95% Ar 5% CH_4	2.7	0.1 to 100 ppb
Holdren and Spicer, 1984	5 ft x 1/8 in Teflon	60/80 Mesh Carbowax 600	Gas Chrom Z	35	70	90% Ar 10% CH_4	3.00	ppb range
Peake and Sandhu, 1983	3.3 ft x 1/8 in Glass	5% Carbowax 600	Chromosorb W	33	50	N_2	N.A.	0.2 to 20 ppb
Singh and Salas, 1983	1.2 ft x 1/8 in Teflon	10% Carbowax 600	80/100 Mesh Supelcoport	33	30	95% Ar 5% CH_4	N.A.	0.02 to 0.10 ppb
Grosjean et al., 1984	1.7 x 1/8 in Teflon	10% Carbowax 400	60/80 Mesh Chromosorb G	30	40	N_2	5.0	2 to 400 ppb
Nielson et al., 1982	3.9 ft x 1/12 in Glass	5% Carbowax 400	Chromosorb W - AW - DCMS	25	40	N_2	6.0	11 ppb

of air was collected by preconcentration into an unpacked 0.15 cm o.d. stainless tube of 1.24 ml volume, at liquid argon temperature, prior to analysis (see Table 5-12). For measurements in humid environments, the air sample was passed through a Nafion drier (Foulger and Simmonds, 1979) to reduce the humidity prior to preconcentration. A minimum detection limit of 0.010 ppb was obtained. Free tropospheric concentrations in the 0.010 to 0.100 ppb range were always observed and indicated that PAN is a natural constituent of the atmosphere and may constitute a significant fraction of the reactive nitrogen.

There are conflicting reports in the literature on the effects of variable relative humidity on PAN measurements by GC-ECD. In 1973, Stephens and Price stated that in preparing PAN calibration samples "the diluent (gas) should be of normal humidity so that the chromatogram will be a realistic one." The reason(s) for this precaution were not given. Subsequently, Holdren and Rasmussen (1976) observed a reduced response to PAN calibration samples when the relative humidity of the sample was 30 percent or lower and a tenfold decrease in PAN response when the relative humidity approached 0 percent. This effect was attributed to an interaction between sample and GC column. Nieboer and van Ham (1975) reported that "the elution gas stream was previously humidified . . . because it appeared that the height of the PAN peak depends on the relative humidity of ambient air if dry elution gas was used." In contrast to these studies, Lonneman (1977) observed no effect on peak height in PAN calibration samples in which the relative humidity varied from 10 to 50 percent.

In 1978, Watanabe and Stephens reported on a reexamination of the moisture anomaly and investigated the effects of humidity on PAN storage flasks, columns, and detectors. A consistent PAN loss to the walls of dry acid-washed glass storage flasks was observed. This PAN could be recovered by the addition of moisture to the flasks. A tritium direct-current detector showed no humidity effect except for a small (5 to 10 percent) decrease in peak height in a few cases at very low humidities (2 to 3 percent). With a different GC instrument employing a Ni-63 detector, erratic responses were observed at low humidities, with responses reduced 30 to 95 percent from that obtained at 53 percent relative humidity. No conclusion was drawn on whether this difference reflected a humidity effect on the detector, the column, or the sampling value. Finally, the moisture anomaly did not appear to depend on column history or loading even after a bake-out treatment.

In the most recent study (Grosjean et al., 1984), the humidity effect on PAN calibration samples prepared by the dynamic and static irradiation of $CH_3CHO-Cl_2-NO_2$ mixtures was examined. A small decrease ($\leq$3 percent) was observed in PAN peak height when the dry air stream was passed either over an impinger containing water or directed through the water impinger. These results are in contradiction to all of the above, in which the response to humidified PAN samples is either greater than or the same as dry PAN samples.

It is noteworthy that the chromatographic systems employed by different investigators often employ different materials of construction (e.g., glass, Teflon, stainless steel), column loadings, and detectors. The resolution of all the differences noted above in regard to a suspected humidity effect might require considerable effort. For the present, if a moisture effect is suspected in a PAN analysis, the bulk of this evidence suggests that humidification of PAN calibration samples (to a range approximating the humidity of the samples being analyzed) would be advisable.

Conventional long-path infrared spectroscopy and Fourier-transform infrared spectroscopy (FTIR) have been used to detect and measure atmospheric PAN. Sensitivity is enhanced by the use of FTIR over conventional long-path infrared spectroscopy. Accurate knowledge of the absorptivities of many IR bands assignable to PAN makes possible the quantitative analysis of PAN without the use of calibration standards. The most frequently used IR bands have been assigned and the absorptivities shown in Table 5-13 have been reported. Only the key bands are shown, but all 27 fundamentals are infrared active and Bruckmann and Willner (1983) have assigned most of them. The assignment by Adamson and Guenthard (1980) of the bands at 1435, 1300, and 990 cm^{-1} to an impurity, CH_3ONO_2, is apparently incorrect. Bruckmann and Willner (1983) observed these same bands in a 99 percent pure PAN sample.

The initial discovery of PAN in simulated photochemical smog was accomplished by long-path infrared absorption spectrometry (Stephens et al., 1956). Some recent simultaneous measurements of PAN and other atmospheric pollutants such as O_3, HNO3, HCOOH, and HCHO have been made by long-path FTIR spectrometry during smog episodes in the Los Angeles Basin. Tuazon et al. (1978) have described an FTIR system operable at pathlengths up to 2 km for ambient measurements of PAN and their trace constituents. This system employed an eight-mirror multiple reflection cell with a 22.5-m base path. The spectral windows available at pathlengths of 1 km were 760-1300, 2000-2230, and 2390-3000 cm^{-1}. Thus, PAN

TABLE 5-13. PAN INFRARED ABSORPTIVITIES

		Absortivity, ppm^{-1} m^{-1} x 10^4				
Frequency, cm^{-1}	Mode	Liquid PAN (Bruckmann and Willner, 1983)	PAN in air (Stephens, 1969)	Frequency, cm^{-1}	PAN in air (Stephens and Price, 1973)	PAN in octane (Holdren and Spicer, 1984)
1842	$\nu(c{=}o)$	12.4	10.0	1830	10.0	9.44
1741	$\nu_{as}(NO_2)$	32.6	23.6	1728	23.6	26.5
1302	$\nu_s(NO_2)$	13.6	11.2	1294	11.4	9.44
1162.5	$\nu(c{-}o)$	15.8	14.3	1153	13.9	9.66
930	$\nu(o{-}o)$	N.A.[a]	N.A.[a]	930	1.8	N.A.[a]
791.5	$\delta(NO_2)$	13.4	10.1	787	10.3	10.1

[a] Not available.

could be detected by the bands at 793 and 1162 cm^{-1}. The 793 cm^{-1} band is characteristic of peroxynitrates, while the 1162 cm^{-1} band is reportedly caused by PAN only (Hanst et al., 1982). Tuazon et al. (1981) reported on ambient measurements with his systems taken during a smog episode in Claremont, CA, in 1978. Maximum PAN concentrations ranged from 6 to 37 ppb over a 5-day episode; the report presented diurnal patterns for PAN and several other pollutants for the 2 most severe days. The detection limit given for PAN at a 900-m pathlength was 3 ppb.

Hanst et al. (1982) modified the FTIR system used by Tuazon et al. (1978) by changing it from an eight-mirror to a three-mirror cell configuration and by considerably reducing the cell volume. Measurements were made over a 1260-m optical path folded along a 23-m base path at 0.25 cm^{-1} resolution. Measurements were reported for PAN and a variety of other pollutants for a 2-day smog episode at California State University, Los Angeles, in 1980. The maximum PAN concentration observed was 15 ppb for this period of only moderate smog intensity. An upper limit of 1 ppb of peroxybenzoyl nitrate (PbzN) was placed based on observations in the vicinity of the PBzN band at 990 cm^{-1}. The reports by Tuazon et al. (1978) and Hanst et al. (1982) both refer to earlier FTIR ambient air studies.

Sampling may constitute one of the major problems in the analysis of trace reactive species, such as PAN, by long-path FTIR spectrometry. The folded-path White cells have a significant internal volume (15 m^3 for Tuazon et al., 1979; 3 m^3 for Hanst et al., 1982). The large internal surface area may serve to promote the decomposition or irreversible adsorption of reactive, trace species. To minimize these effects, both Tuazon et al. and Hanst et al. employed high-speed blowers to pull ambient air through the cells at high velocities. For interior cell linings, Hanst et al. employed 0.5 mm polyvinyl chloride sheeting and Tuazon et al. used Plexiglas and FEP Teflon.

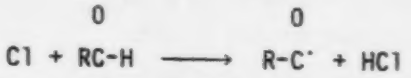
Pitts et al. (1973) proposed a chemiluminescence technique for continuous monitoring of ambient concentrations of PAN. The reactions of both PAN and O_3 with triethylamine in the gas phase produce chemiluminescence. The spectra reported overlap somewhat with a λ_{max} of 520 nm for the O_3 reaction and λ_{max} of 650 nm for the PAN reaction. Pitts proposed a technique whereby, through measurement of the emission intensity in the two regions by the use of optical cut-off filters, the PAN concentration could be determined, provided simultaneous measurements were made of the absolute O_3 concentration. Concentrations of 6 ppb PAN were detected and a lower limit of detection of 1 ppb was estimated. No interfering emissions were observed from methyl nitrate, ethyl nitrate, ethyl nitrite, or NO_2. No further work has been reported on the development of this technique, and there have not been any atmospheric applications.

5.5.7.3 Generation and Calibration. Because of the thermal instability of dilute PAN samples and the explosive nature of purified PAN, calibration samples are not available, and each laboratory involved in making such measurements must prepare its own standards. The PAN samples are prepared by various means at concentrations in the ppm range and these must be analyzed by some absolute technique. The analyzed samples must then be diluted to obtain gas-phase samples in the low ppb range for direct calibration of GC instruments. Thus, the following section includes descriptions of various means of PAN generation, methods of analysis, and the procedures for sample handling and storage where applicable.

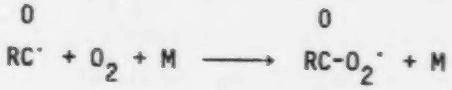
The earlier methods used for the preparation of PAN have been summarized by Stephens (1969). These included (1) the photolysis of mixtures of nitrogen oxides with organic compounds in air or oxygen (Stephens, 1956; Stephens et al., 1961); (2) the photolysis of alkyl nitrite vapor in oxygen (Stephens et al., 1965); (3) the dark reaction of aldehyde vapor with nitrogen pentoxide (Tuesday, 1961); and (4) the nitration of peracetic acid. Of these methods, the photolysis of alkyl nitrites was favored and used extensively by Stephens and other investigators. As described by Stephens et al. (1965), the liquefied crude mixture obtained at the outlet of the photolysis chamber is purified by preparation-scale GC. [CAUTION: Both the liquid crude mixture and the purified PAN samples are violently explosive and should be handled behind explosion shields using plastic full-face protection, gloves, and a leather coat at all times. These PAN samples should be handled in the frozen state whenever possible.] The pure PAN is usually diluted to about 1000 ppm in nitrogen cylinders at 100 psig. When refrigerated at $\leq$15°C, PAN losses are less than 5 percent per month (Stephens et al., 1965). Lonneman et al. (1976) used the photolysis products without purification for the calibration of GC instruments in the field and discussed the use of Tedlar bags for the preparation and transport of calibration samples.

Gay et al. (1976) have used the photolysis of Cl_2: aldehyde: NO_2 mixtures in air or oxygen for the preparation of PAN and a number of its homologues at high yields:

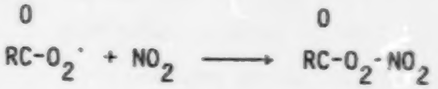
$$\mathrm{Cl_2 + h\nu \longrightarrow 2\ Cl} \qquad (5\text{-}79)$$



$$\mathrm{Cl + R\overset{O}{C}{-}H \longrightarrow R{-}\overset{O}{C}{}^{\cdot} + HCl} \qquad (5\text{-}80)$$



$$\mathrm{R\overset{O}{C}{}^{\cdot} + O_2 + M \longrightarrow R\overset{O}{C}{-}O_2{}^{\cdot} + M} \qquad (5\text{-}81)$$



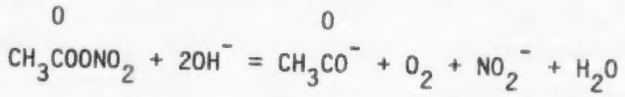
$$\mathrm{R\overset{O}{C}{-}O_2{}^{\cdot} + NO_2 \longrightarrow R\overset{O}{C}{-}O_2{-}NO_2} \qquad (5\text{-}82)$$

This procedure has been utilized in a portable PAN generator that can be used for the calibration of GC-ECD instruments in the field (Grosjean, 1983; Grosjean et al., 1984). The output of this generator is a dynamic flow of PAN in air at a concentration of about 2 to 450 ppb. Dilute concentrations of reactant gases for the photolysis chamber are obtained by passing a controlled flow of air over Cl_2, NO_2, and acetaldehyde permeation tubes.

The other technique for PAN preparation in current use involves the nitration of peracetic acid. In the 1969 review (Stephens, 1969), this approach was considered not useful for synthesis. Several investigators, however, have recently reported on a condensed-phase synthesis of PAN with peracetic acid that produces high yields of a pure product free of other alkyl nitrates (Hendry and Kenley, 1977; Kravetz et al., 1980; Nielsen et al., 1982; Holdren and Spicer, 1984). Most of these procedures call for the addition of peracetic acid (40 percent in acetic acid) to a hydrocarbon solvent (pentane, heptane, octane) maintained at 0°C in a dry-ice acetone bath, followed by acidification with sulfuric acid. Nitric acid is formed *in situ* with stirring by the slow addition of sodium nitrate. After the nitration is complete, the hydrocarbon fraction, containing PAN concentrations of 2 to 4 mg/ml (Nielsen et al., 1982), can be stored at -20°C for periods longer than a year (Holdren and Spicer, 1984). After analysis, the PAN-hydrocarbon solutions can be used directly for calibration by the evaporation of measured microliter volumes of solution into Tedlar bags containing known volumes of clean air.

The most direct method for absolute analysis is by infrared absorption using absorptivities given in Table 5-13. This is the technique used by Stephens (1969; analysis of PAN in N_2 cylinders), Lonneman et al. (1976; analysis of gas-phase products from photolysis of ethyl nitrite); and Holdren and Spicer (1984; analysis of PAN in octane solutions). Whereas long, folded-path cells and FTIR spectrometry are required for the analysis of atmospheric PAN, conventional IR instruments and 10-cm gas cells can analyze gas standards with concentrations greater than 35 ppm (Stephens, 1969) and Holdren and Spicer (1984) used 50-μm liquid microcells for the analysis of PAN in octane solutions. Another candidate technique for absolute PAN analysis is gas-phase coulometry using a tandem electron-capture detector (Lovelock et al., 1971). Singh and Salas (1983) have shown, however, that this technique is unsuitable for absolute PAN analysis because a significant fraction of the PAN is destroyed prior to coulometric detection.

The alkaline hydrolysis of PAN to acetate ion and nitrite ion in quantitative yield (Nicksic et al., 1967) provides a means independent of infrared for the quantitative analysis of PAN. Molecular oxygen is also produced in quantitative yield by the reaction (Stephens, 1967):



$$CH_3\overset{O}{C}OONO_2 + 2OH^- = CH_3\overset{O}{C}O^- + O_2 + NO_2^- + H_2O \qquad (5\text{-}83)$$

The colorimetric determination of nitrite ion with Saltzman reagent was first used to measure PAN quantitatively (Stephens, 1969; Kravetz et al., 1980). Nielsen et al. (1982) analyzed the hydrolyzed products of pure PAN samples by ion chromatography for nitrite and nitrate and found that 4 percent of the nitrite had been oxidized to nitrate. Some gas-phase PAN calibration samples (e.g., photolysis of Cl_2: acetaldehyde: NO_2) contain impurities such as NO_2 that will yield nitrite and nitrate in aqueous solution. Thus, Grosjean (1983) and Grosjean et al. (1984) performed ion chromatographic analysis of the acetate ion to determine the PAN output of a portable generator.

An alternate calibration procedure has been proposed based on the thermal decomposition of PAN in the presence of excess NO (Lonneman et al., 1982; Lonneman and Bufalini, 1982). The peroxy radical, $CH_3C(O)O_2$, and its decomposition products rapidly oxidize NO to NO_2. In the presence of a small amount of benzaldehyde, which is used to scavenge the hydroxyl radical and control the stoichiometry, simulation models predict that 5 molecules of NO will be removed per PAN molecule present. By the use of NO and PAN standard mixtures and the chemiluminescent measurement of the NO consumed, the experimental value was determined to be $\Delta NO/\Delta PAN = 4.7 \pm 0.2$. While it will not give the precision of which the techniques above are capable, this measurement could be performed in field stations where chemiluminescent NO analyzers are usually available.

5.5.7.4 Methods of Analysis of Higher Homologues. The GC-ECD analyzer is likewise used for the higher homologues of PAN (Darley et al., 1963; Stephens, 1969; Heuss and Glasson, 1968). The higher homologues elute with longer retention times. The first observation of PPN in heavily polluted air was by Darley et al. (1963) who also measured peroxybutyryl nitrate in synthetic mixtures by GC-ECD. The concentrations of the higher homologues in ambient air are usually below the detection limits of the GC-ECD technique. Heuss and Glasson (1968) measured PBzN in irradiated auto exhaust samples by GC-ECD and reported that this homologue was 100 times more potent than PAN as a lachrymator. The direct analyses of PBzN by GC-ECD is reported to be complicated by interferences (Appel, 1973). Therefore, an analytical technique was developed in which the PBzN was quantitatively hydrolyzed to methyl benzoate (MeOBz), followed by GC analysis for MeOBz using a flame ionization detector (Appel, 1973). An upper limit of 0.07 ppb was placed on the concentration of PBzN in the San Francisco bay area. The analysis for the higher homologues of PAN in the atmosphere by FTIR spectrometry is not feasible because of inadequate sensitivity, although Hanst et al. (1982) placed an upper limit for PBzN in smoggy Los Angeles air of 1 ppb based on absorption in the 990 cm^{-1} region.

The higher homologues of PAN may be prepared in the same manner as PAN by the use of a compound containing the parent alkyl group. Thus, PPN and PBzN have been prepared by the photolysis of alkyl nitrates in oxygen (Stephens, 1969) and parent aldehydes plus chlorine and NO_2 (Gay et al., 1976). The study of Gay et al. (1976) confirmed that the first member of the series, peroxyformyl nitrate $[HC(O)O_2NO_2]$, is too unstable to be observed. There have been few reports of the absolute analysis for the higher homologues. Infrared absorption analysis of purified samples should be the preferred technique. Infrared absorptivities of homologues have been reported by Stephens (1969) and Gay et al. (1976).

5.5.8 Methods for Sampling and Analysis of Hydrogen Peroxide

5.5.8.1 Introduction. Hydrogen peroxide (H_2O_2) is expected to be mechanistically significant in photochemical smog as a chain terminator and as an index of the hydroperoxyl radical (HO_2) concentration (Bufalini, 1969; Demerjian et al., 1974). The major reaction leading to the formation of H_2O_2 is the recombination of the hydroperoxyl radical (Graedel, 1976):

$$HO_2^{\cdot} + HO_2^{\cdot} + M = H_2O_2 + O_2 + M \qquad (5\text{-}84)$$

Recent studies have implicated atmospheric H_2O_2 in the aqueous-phase oxidation of SO_2 to SO_4^{-2} and in the acidification of rain (Penkett et al., 1979; Dasgupta, 1980; Martin and Damschen, 1981; Overton and Durham, 1982). (As described in chapter 4, however, it is not the predominant mechanism, since the OH radical appears to be the main agent for the homogeneous gas-phase oxidation of SO_2 to SO_3^-, which is subsequently oxidized to SO_4^-).

Some controversy appears to exist concerning the time and concentration correlation between H_2O_2 and O_3. If this correlation could be assessed, then the concentration of H_2O_2 could be predicted from the concentration of O_3. According to one report (Gay and Bufalini, 1972), the H_2O_2 concentration reached a maximum of 0.18 pphm at the same time as the O_3 maximum of 0.65 pphm (at 3:00 pm) in the urban atmosphere of Riverside, California. On the other hand, Kok et al. (1978a) did not observe any definitive correlation between O_3 and H_2O_2 in the same area. This discrepancy may result in large part from the use of different measurement methods. One of the major problems in assessing the role of atmospheric H_2O_2 has been a lack of adequate measurement methodology. Suitable techniques may now be available for aqueous H_2O_2, but recent studies (Zika and Saltzman, 1982; Heikes et al., 1982) have cast doubt on the validity of methods for atmospheric H_2O_2 that use aqueous sampling because of interfering reactions of absorbed O_3. Techniques that have been used or proposed for aqueous- and gas-phase H_2O_2 are discussed below, as well as methods for sampling, generation, and standardization of H_2O_2 samples.

5.5.8.2 Sampling. Almost all of the methods used for the measurement of atmospheric H_2O_2 have used aqueous traps for sampling. In the method used by Kok et al. (1978b), atmospheric samples containing H_2O_2 were collected in aqueous solution using midget impingers. A continuous extraction process for sampling H_2O_2 from the atmosphere and concentrating it in the aqueous phase for chemiluminescence measurement has also been described by Kok et al. (1978a).

The apparatus used by Zika and Saltzman (1982) to sample H_2O_2 in ambient air consists of two 500-ml fitted gas-washing traps, each containing 500 ml of water, a vacuum pump, and a flow meter. Teflon tubing was used to connect the various components and to draw air into the apparatus. The traps were filled with distilled water and air was drawn through them at a controlled flow rate. At various intervals, the flow was briefly interrupted, and samples were withdrawn from the traps for H_2O_2 analyses. Prior to analysis, samples were degassed with high-purity helium to remove any O_3 that may have been present. The efficiency of the system for extraction of H_2O_2 from the air was tested. The first trap was found to be 99 percent efficient in removing H_2O_2 from the gas stream; and over a concentration range of 10^{-8} to 10^{-3} M, no H_2O_2 was detected in the second trap.

The most serious problem with methods that use aqueous traps is their potential interference from atmospheric O_3, which is present in much higher concentrations. The recent study of Zika and Saltzman has shown that absorbed O_3 leads to both the formation and destruction of H_2O_2 (Zika and Saltzman, 1982). Details of the aqueous chemistry of O_3 can also be found in other sources (Hoigne and Bader, 1976; Kilpatrick et al., 1955; Taube and Bray, 1940). An obvious research need in H_2O_2 measurements is a clear delineation of the nature of any O_3 interferences and the development of means for their prevention.

5.5.8.3 Measurement. A number of methods for measuring low levels of H_2O_2 have been reported, including the following:

1. Titanium colorimetric methods.
2. Chemiluminescence methods.
3. Enzyme-catalyzed methods.
4. Fourier-transform infrared method.
5. Electrochemical methods.
6. H_2O_2-olefin reaction.
7. Mixed-ligand complexes.
8. Iodometry.

Of these, techniques 1 through 3 above have been used for atmospheric analysis and will be emphasized. Methods 4 through 7 have not been used for atmospheric analysis and will be only briefly summarized. Iodometric techniques are useful only for calibration and will be discussed in that section.

5.5.8.3.1 Titanium colorimetric methods. The titanium sulfate-8-quinolinol reagent method has been used in several studies on atmospheric H_2O_2 (Bufalini et al., 1972; Gay et al., 1972a; Gay et al., 1972b; Kok et al., 1978a). Hydrogen peroxide in air is scrubbed in a coarse-fritted bubbler containing aqueous titanium sulfate-ammonium sulfate-sulfuric acid solution at a concentration of approximately 50 µg/ml of titanium (IV). After sampling, the pH of the solution is adjusted to 4.2 ± 0.2 and the mixture is extracted with an aliquot of 0.1 percent 8-quinolinol in chloroform. The absorbance at 450 nm of the titanium (IV)-H_2O_2-8-quinolinol complex in chloroform is determined.

This method has the following advantages. The molar absorptivity of the titanium(IV)-H_2O_2-8-quinolinol complex at 450 nm is 3060 $M^{-1}cm^{-1}$; i.e., the method is very sensitive. The time between sample preparation and absorbance readings can be short. At pH 4.2 ± 0.2, the stoichiometry of the titanium (IV)-H_2O_2 complex is 1 to 1 (Babko and Volkova, 1951). The major disadvantage of the method is that the 8-quinolinol reagent is highly pH-sensitive; i.e., the absorption maximum occurs in a narrow pH range of 4 to 5. The linear dynamic range of Beer's law for this method lies between 0 and 6 µg/ml. The sensitivity of this method is 1.6×10^{-6} M per 0.005 absorbance unit in a 1-cm cell.

A positive interference is expected from any compound that can liberate H_2O_2 via acid hydrolysis (Pobiner, 1961). Accordingly, t-butyl hydroperoxide gives rise to the titanium(IV)-H_2O_2 complex. Of the major atmospheric pollutants investigated (SO_2, O_3, NO_2, NO, and hydrocarbons), only SO_2 at high concentrations gave a small (0.7 percent) negative interference (Gay et al., 1972b). Other compounds tested by Cohen and Purcell (1967)--peracetic acid, ethyl hydroperoxide, n-butyl hydroperoxide, acetyl peroxide, and peroxyacetyl nitrate (PAN)--were found to give slight negative interferences at high concentrations.

The titanium tetrachloride method of analysis for hydrogen peroxide is described by Pilz and Johann (1974) and Kok et al. (1978a). Samples are collected in a midget impinger containing an aqueous titanium tetrachloride-hydrochloric acid ($TiCl_4$-HCl) solution at a concentration of approximately 8 mg/ml of titanium(IV). A stable $TiCl_4$-H_2O_2 complex is formed immediately, and, after dilution to a known volume, the absorbance of the complex at 410 nm is determined (molar absorptivity = 735 $M^{-1}cm^{-1}$). For H_2O_2 concentrations less than 100 ppb, 5-cm cells and 0.05 absorbance full-scale were used. The principal difficulty with this method is the formation of fine particles, presumably TiO_2, in solution. The presence of suspended precipitate scatters visible radiation and creates an apparent absorption. Another problem is that the reagent is quite acidic and hygroscopic. Kok et al. (1978a) has compared measurements with both titanium reagents and chemiluminescence.

5.5.8.3.2 Chemiluminescence. Hydrogen peroxide in the atmosphere may be detected at low concentrations by the chemiluminescence obtained from Cu(II)-catalyzed oxidation of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) by H_2O_2 (Armstrong and Humphreys, 1965). The reagent is a solution containing luminol, 1 x 10^{-5} M Cu(II), and NaOH (pH = 12.8). The products of the reaction with H_2O_2 are 3-amino-phthalic acid, a nitrogen molecule, and a photon of light at 450 nm. The detection limit for atmospheric samples has been given as 0.001 ppm, and the linear dynamic range is 0.001 to 1 ppm.

A small positive interference was reported for PAN (Kok et al., 1978b). If O_3 absorption leads to the formation of H_2O_2 (Zika and Saltzman, 1982; Heikes et al., 1982), as reported, then O_3 is a major interference. There have also been undocumented reports of a negative interference from SO_2. The exact mechanism of the chemiluminescent oxidation of luminol is not known, but involves the decomposition of H_2O_2 by the copper (II) catalyst (Delumyea, 1974; Burdo and Seitz, 1975).

5.5.8.3.3 Enzyme-Catalyzed Methods (Peroxidase). This general method involves three components: a substrate that is oxidizable; the enzyme, horseradish peroxidase (HRP); and H_2O_2. The production or decay of the fluorescence intensity of the substrate is measured as it is oxidized by H_2O_2, catalyzed by HRP. Some of the more widely used chromogenic substrates are scopoletin (6-methoxy-7-hydroxy-1,2-benzopyrone) (Andreae, 1955; Perschke and Broda, 1961); 3-(p-hydroxyphenyl)propionic acid (HPPA) (Zaitsu, 1980); and leuco crystal violet (LCV) (Mottola et al., 1970).

In the scopoletin method, the reagent solution is mixed with a second solution containing the H_2O_2, the concentration of which must not be less than 0.33 nor more than 0.84 times the concentration of scopoletin (Perschke and Broda, 1961). The disappearance of scopoletin fluorescence is monitored and the fluorescence intensity can be used to obtain the concentration of H_2O_2 from a calibration curve. The most significant advantages of this method of analysis are the specificity for H_2O_2, the sensitivity, and the stoichiometry of the scopoletin:H_2O_2 reaction (1:1 mole per mole as long as scopoletin is present in a 20-fold excess over HRP). Ascorbic acid, glutathione, and manganous ions are reported to inhibit the oxidation of scopoletin by peroxidase (Andreae, 1955). As the pH of the mixture deviates from 10, the method produces less reliable results. The chief disadvantage of the scopoletin method is that the concentration of H_2O_2 must be within a narrow range in order to obtain an accurately measurable decrease in fluorescence. This limits the usefulness of the technique in determining unknown H_2O_2 concentrations over several orders of magnitude (Armstrong and Humphreys, 1965; Andreae, 1955). Detection limits for this technique are quite low and are in the range of 1.5 x 10^{-11} M (Perschke and Broda, 1961) to 2 x 10^{-10} M (Andreae, 1955).

With the leuco crystal violet (LCV) substrate, intensely colored crystal violet is formed from the reaction of H_2O_2 with LCV, catalyzed by HRP. In the method described by Mottola et al. (1970), the substrate is added to an aqueous sample containing H_2O_2. Upon addition of a solution of HRP, the solution turns violet. The absorbance is measured at 596 nm, where the absorption coefficient of crystal violet is 10^5 $M^{-1}cm^{-1}$, a very high value and an inherent advantage of this method. The concentration of H_2O_2 is a linear function of the concentration of crystal violet produced. The detection limit reported is about 10^{-8} M H_2O_2 for an absorbance of 0.005 in a 5-cm cell.

The HRP catalyzes the oxidation of a wide variety of hydrogen-donating substrates by H_2O_2. Zaitsu and Ohkura (1980) have tested a number of 4-hydroxyphenyl compounds and found that 3-(p-hydroxyphenyl) propionic acid (HPPA) provided the most sensitive and rapid means for determining H_2O_2. When HPPA reagent solution is mixed with HRP solution and a test solution containing H_2O_2, a product is formed that fluoresces at 404 nm following excitation at 320 nm. The intensity of this fluorescence is monitored as a function of H_2O_2 concentration. The detection limit was reported to be 10^{-10} mole H_2O_2 with a linear range extending to 10^{-8} mole H_2O_2 when a test solution of only 0.1 ml volume was used. Presumably the molar sensitivity could be improved by the use of larger sample volumes. No interference studies were reported.

The enzymatic methods appear to be the most promising aqueous, colorimetric methods for H_2O_2 and have considerably greater sensitivity than the methods employing titanium reagents. Studies of potential atmospheric interferences, however, have not been reported for any of these three substrates.

5.5.8.3.4 Other Methods. Hydrogen peroxide has been monitored in the gas phase at ppm concentrations in laboratory mechanistic studies by the use of long-path

FTIR absorption using the H_2O_2 band in the region, 1200-1350 cm^{-1} (Su et al., 1979; Niki et al., 1980). The band most suitable for quantitative analysis is centered at 1267 cm^{-1}. The infrared absorptivity at 1250 cm^{-1} has recently been measured and a value of 8.4 cm^{-1} atm^{-1} obtained at 1-cm resolution (Hanst et al., 1981). An attempt was made to observe H_2O_2 absorption during an intense smog episode in Pasadena, California, and the possible presence of 0.070 ppm H_2O_2 was reported (Hanst et al., 1975). Unfortunately, the minimum detection limits in this region are severely compromised by neighboring absorption bands of H_2O and CH_4. Hanst et al. (1981) have discussed the problems with FTIR measurements of H_2O_2 and have assigned a minimum detection limit of 0.040 ppm for a 1-km total pathlength. Thus, concentrations of H_2O_2 as high as 0.010 to 0.030 ppm would not be detectable by FTIR as currently used.

The redox system, O_2/H_2O_2, lends itself to electrochemical analysis. This system is complex because of the presence of three related redox systems: O_2/H_2O_2, H_2O_2/H_2O, O_2/H_2O. Accordingly, to determine the concentration of H_2O_2 in aqueous media, the indicator electrode must be adequately specific toward the O_2/H_2O_2 redox system. Pisarevskii and Polozova (1980) used a modified graphite electrode (MGE) consisting of a thin layer of graphite etched onto electron-conducting silicate glasses. With a reference electrode of Ag/AgCl/KCl (saturated), H_2O_2 could be measured over the range of 5×10^{-6} M to 1 M.

Hauser and Kolar (1968) reported an interference from H_2O_2 in the reaction between O_3 and 1,2-di-(4-pyridyl)ethylene (DPE) and investigated this reaction for the measurement of H_2O_2. The reaction of DPE with O_3 or H_2O_2 produces pyridine-4-aldehyde, which may be analyzed colorimetrically with 3-methyl-2-benzothiazolinone hydrazone (MBTH) reagent. The detection limit reported for H_2O_2 was approximately 10^{-6} M with a linear range extending to about 5×10^{-4} M. No atmospheric applications have been reported. Atmospheric O_3 would be a major interference.

Mixed-ligand complexes of the type $M:L:H_2O_2$ provide sensitive means for the determination of H_2O_2. In particular, vanadium(V)-xylenol orange (XO) chelates, vanadium hydroxamic acid chelates, and uranium hydroxamic acid chelates provide good examples of sensitive mixed ligands (Csanyi, 1981; Meloan, 1961). A vanadium(V)-XO reagent can be used for the spectrophotometric determination of 10^{-6} M concentrations of H_2O_2 (Csanyi, 1981). Methods using vanadium hydroxamic acid chelates (VHAC) (I) and uranium hydroxamic acid chelates (UHAC) (II) measure the concentration of the chelate remaining after reaction between the chelate and H_2O_2. These methods are reportedly specific for H_2O_2. The following alkyl peroxides were found not to interfere in the determination of H_2O_2: tert-butyl peroxide, di-tert-butyl peroxide, tert-butyl perbenzoate, hydroxyheptyl peroxide, and lauroyl peroxide (Meloan et al., 1961). This method can be used to detect a total concentration of 7×10^{-6} mole of H_2O_2 if the uranium system is used and 1×10^{-6} mole if vanadium is used. Interferences can be expected among other strong oxidizing agents that are water-soluble and are extracted into the aqueous phase along with H_2O_2.

5.5.8.4 Generation and Calibration Methods

5.5.8.4.1 Generation. Standard samples containing trace concentrations of H_2O_2 are required for testing and calibration of various measurement methodologies. As with O_3, such standards are not available and are usually prepared at the time of use. A number of techniques have been employed for generating aqueous standards, but convenient methods for the generation of gas-phase standards are noticeably lacking.

Techniques for the generation of high concentrations of H_2O_2 have been discussed by Shanley (1948). Commercial solutions of 30 percent aqueous H_2O_2 are readily available. Trace levels of H_2O_2 in water may be generated by the irradiation of water with ^{60}CO γ-radiation (Hochanadel, 1952; Armstrong and Humphreys, 1965) and by enzymatic means (Andreae, 1955). By far the most convenient method for generating aqueous standards containing micromolar concentrations of H_2O_2 is simply the serial dilution of commericial-grade 30 percent H_2O_2 (Fisher Analytical Reagent). Samples prepared in this manner must be standardized and the method usually employed is the iodometric technique discussed below. Stock standard solutions of H_2O_2 as low in concentration as 10^{-4} M have been found to be stable for many weeks if kept in the dark (Armstrong and Humphreys, 1965).

Techniques for the convenient generation of gas-phase standards are not available. With the increased interest in atmospheric H_2O_2, there is an obvious need for an H_2O_2 generator comparable to the photolytic O_3 generator discussed in section 5.5.5.1. A technique that has often been used for generating ppm concentration levels of H_2O_2 in air has been described by Cohen and Purcell (1967). Microliter quantities of 30 percent H_2O_2 solution are injected into a metered stream of air that flows into a Teflon bag. The concentration of H_2O_2 in the bag is then determined by the iodometric method discussed below.

5.5.8.4.2 Calibration. By far the most common method for standardizing low concentrations of H_2O_2 is based on iodometry (Allen et al., 1952; Hochanadel, 1952; Cohen et al., 1967). Hydrogen peroxide liberates iodine from an iodide solution quite slowly, but in the presence of a molybdate catalyst the reaction is quite rapid. The iodine liberated may be determined by titration with standard thiosulfate at higher concentrations or by photometric measurement of the tri-iodide ion at low concentrations. The molar absorption coefficient of the tri-iodide ion at 350 nm has been determined to be 2.44×10^4 by measuring 10^{-5} to 10^{-4} M H_2O_2 solutions prepared from 0.2 M stock H_2O_2 solution standardized against primary grade arsenious oxide (Armstrong and Humphreys, 1965). The stoichiometry is apparently 1 mole of iodine released per mole of H_2O_2. Definitive studies of the stoichiometry, however, have not been performed to the same extent as those of the stoichiometry for the iodometric determination of O_3.

5.6 SUMMARY

5.6.1 Properties

Ozone, peroxyacetyl nitrate, and hydrogen peroxide, along with other photochemical oxidants occurring at very low concentrations in ambient air, are characterized chiefly by their ability to remove electrons from or to share electrons with other molecules or ions (i.e., oxidation). The capability of a chemical species for oxidizing or reducing other chemical species is termed "redox potential" (positive or negative standard potential) and is expressed in volts. Ozone has a standard potential of +2.07 volts in aqueous systems (for the redox pair, O_3/H_2O). Hydrogen peroxide has a standard potential of +1.776 in the redox pair, H_2O_2/H_2O. No standard potential for peroxyacetyl nitrate in neutral or buffered aqueous systems, such as those that occur in biological systems, appears in the literature. In acidic solution (pH 5 to 6), PAN hydrolyzes fairly rapidly; in alkaline solution it decomposes with the production of nitrite ion and molecular oxygen.

The toxic effects of oxidants are attributable to their oxidizing ability. Their oxidizing properties also form the basis of the measurement techniques for all three of these pollutants. The calibration of ozone and PAN measurements, however, is achieved via their spectra in the ultraviolet and infrared, respectively. The calibration of measurement methods for H_2O_2 is achieved with iodometric techniques that depend on the oxidizing properties of H_2O_2.

An important property of PAN, especially in the laboratory, is its thermal instability. Its explosiveness dictates its synthesis for calibration purposes by experienced personnel only. All three pollutants must be generated in situ for the calibration of measurement techniques. For ozone and H_2O_2, generation of calibration gases is reasonably straightforward.

5.6.2 Reactions of Ozone and Other Oxidants in Ambient Air

The atmospheric reactions of ozone and of other photochemical oxidants such as peroxyacetyl nitrate (PAN) and hydrogen peroxide (H_2O_2) are complex and diverse, but are becoming increasingly well-characterized. The reactions of these species result in products and processes that may have significant environmental and health- and welfare-related implications, including effects on biological systems, nonbiological materials, and such phenomena as visibility degradation and acidification of cloud and rain water. Ozone may play a role in the oxidation of SO_2 to H_2SO_4, both indirectly in the gas phase (via formation of OH radicals and Criegee biradicals) and directly in aqueous droplets. Evidence is also accumulating that hydrogen peroxide, like ozone, is involved in both gas-phase photochemistry and aqueous-phase oxidations. For example, studies of the rates of oxidation of SO_2 by H_2O_2 in solution suggest that this reaction is sufficiently fast that it could be the major aqueous-phase route for the oxidation of SO_2 under certain atmospheric conditions. In addition, the importance of oxidants such as PAN in various aspects of atmospheric chemistry, such as long-range transport of NO_x and multi-day air pollution episodes, is now being recognized.

Ozone can react with organic compounds in the troposphere. It is important to recognize, however, tht organics undergo competing reactions with OH radicals in the daytime (Atkinson et al., 1979; Atkinson and Lloyd, 1984) and, in certain cases, with NO_3 radicals during the night (Japar and Niki, 1975; Carter et al., 1981a; Atkinson et al., 1984a,b,c,d), as well as photolysis. Only for organics whose ozone reaction rate constants are greater than $\sim10^{-21}$ cm^3 molecule $^{-1}$ sec^{-1} can consumption by ozone be considered to be atmospherically important (Atkinson and Carter, 1984).

Ozone reacts rapidly with the acyclic mono-, di-, and tri-alkenes and with cyclic alkenes. The rate constants for these reactions range from $\sim10^{-18}$ to $\sim10^{-14}$ cm^3 molecule^{-1} sec^{-1} (Atkinson and Carter, 1984), corresponding to atmospheric lifetimes ranging from a few minutes for the more reactive cyclic alkenes, such as the monoterpenes, to several days. In polluted atmospheres, a significant portion of the consumption of the more reactive alkenes will occur via reaction with ozone, rather than with OH radicals, especially in the afternoons during photochemical oxidant episodes. Reactions between ozone and alkenes can result in aerosol formation (National Academy of Sciences, 1977; Schuetzle and Rasmussen, 1978), with alkenes of higher carbon numbers the chief contributors.

Because of their respective rate constants, neither alkanes (Atkinson and Carter, 1984) nor alkynes (Atkinson and Aschmann, 1984) are expected to react with ozone in the atmosphere, since competing reactions with OH radicals have higher rate constants.

The aromatics react with ozone, but quite slowly (Pate et al., 1976; Atkinson et al., 1982), such that their reactions with ozone are expected to be unimportant in the atmosphere. Cresols are more reactive toward ozone than the aromatic hydrocarbons (Atkinson et al., 1982), but their reactions with OH radicals (Atkinson et al., 1978, 1982) or NO_3 radicals (Carter et al., 1981a; Atkinson et al., 1984a) predominate.

For oxygen-containing organic compounds, especially those without carbon-carbon double bonds, reactions with ozone are slow. For carbonyls and ethers (other than ketene) that contain unsaturated carbon-carbon bonds, however, much faster reactions are observed (Atkinson et al., 1981).

The kinetics of the reactions of ozone with a variety of nitrites, nitriles, nitramines, nitrosamines, and hydrazines have been studied (Atkinson and Carter, 1984), but only for the hydrazines are these reactions sufficiently rapid to be of atmospheric importance. Chamber studies have shown that N-nitrosodimethylamine can result from the reaction of ozone with simple hydrazines (Tuazon et al., 1981a). Whether this product would ever be formed by reaction with ozone in the atmosphere obviously depends upon the presence, and level, of the precursor hydrazines in ambient air.

Certain reactions of ozone other than its reactions with organic compounds are important in the atmosphere. Ozone reacts rapidly with NO to form NO_2, and subsequently with NO_2 to produce the nitrate (NO_3) radical and an oxygen molecule. Photolysis of ozone can be a significant pathway for the formation of OH radicals, particularly in polluted atmospheres when ozone concentrations are at their peak.

5.6.3 Reactions of Ozone and Peroxyacetyl Nitrate in Aqueous (Biological) Systems

Both ozone and PAN can react directly and rapidly with many organic molecules, including many types occurring in biological systems. Additionally, active species such as singlet oxygen, hydroxyl radicals, and superoxide are produced either as products of primary reactions or from the decomposition of ozone or PAN in water; these species also have the potential for causing biological damage.

The reactions of ozone with biologically important functional groups have been described in the literature, although such information remains relatively sparse and is based on in vitro work that is not always pertinent to reactions that occur under the conditions of in vivo exposure. Among the functional groups with which ozone reacts relatively rapidly are the carbon-carbon double bonds (alkenic group) found in biologically important compounds such as some of the essential fatty acids and polyunsaturated fatty acids (PUFA) of the kind found in the lipids of cell membranes. Amines are, in general, close to alkenes in their reactivity toward ozone, although amino groups existing as the amide or salt are less susceptible to ozone than unprotected amino groups. Sulfur-containing compounds, such as methionine, can also undergo electrophilic attack by ozone, resulting in the formation of both sulfoxides and sulfones. Under some conditions (e.g., $pH > 9$), ozone is rapidly converted to hydroxyl radicals, which are less selective than ozone in reactions with organic molecules. The conversion of ozone to superoxide ($O_2\cdot$) and hydroperoxy radicals ($HO_2\cdot$) has also been reported.

Aromatic compounds are much less reactive toward ozone than alkenic compounds in aqueous systems. In compounds containing both aromatic and alkenic groups, such as the indole ring of tryptophan, the initial ozone attack occurs exclusively at the alkenic part of the molecule. Aldehydes react with ozone with and without the involvement of oxygen. Either way, acyl hydrotrioxides are formed that subsequently decompose to peroxides and carboxylic acids. Simple ketones react slowly or not at all with ozone.

Reactions between ozone and specific molecules of importance in biological systems have been described in chapter 10.

Knowledge of the solution chemistry of PAN is limited. It is known, however, that PAN can react with alkenes, with sulfur-containing compounds, and with aldehydes. The half-life of PAN in water (pH 7.2) is only about 4.4 minutes. Thus, some of the toxicological effects ascribed to PAN should possibly be attributed to its decomposition products instead.

5.6.4 Sampling and Measurement of Ozone and Other Photochemical Oxidants

The analysis of ozone and other, related atmospheric oxidants includes requirements for representative sampling, specific and sensitive measurement methodologies, methods for the generation of standard samples, absolute methods for the calibration of these standards, and procedures by which to provide quality assurance for the whole measurement process. In the summary presented below, recommended procedures are given for all of these analytical steps. Sampling and quality assurance are discussed in general terms for all of the oxidants. Methods of analysis, sampling, and generation and calibration are discussed specifically for ozone, peroxyacetyl nitrate (PAN) and its homologues, and hydrogen peroxide. Because of the large existing data base that employed measurements for "total oxidants," non-specific iodometric techniques are discussed and compared to current specific O_3 measurements.

5.6.4.1 Quality Assurance and Sampling. A quality assurance program is employed by the U.S. Environmental Protection Agency for assessing the accuracy and precision of monitoring data and for maintaining and improving the quality of ambient air data. Procedures and operational details have been prescribed in each of the following areas: selection of analytical methods and instrumentation (i.e., reference and equivalent methods); method specifications for gaseous standards; methods for primary and secondary (transfer standards) calibration; instrumental zero and span check requirements, including frequency of checks, multiple-point calibration procedures, and preventive and remedial maintenance requirements; procedures for air pollution episode monitoring; methods for recording and validating data; and information on documentary quality control (U.S. Environmental Protection Agency, 1977).

A crucial link in the measurement cycle involves sampling strategies and techniques. Sampling strategies, which involve the design and operation of a sampling network, must be consistent with the specific purpose of the measurements. Ambient air monitoring data are collected for a variety of purposes, each of which may have different requirements that affect sampling strategy. For example, a sampling strategy for health effects research studies may require a number of monitoring stations carefully situated to assess human exposure for a given urban population over a finite period of time. In addition, since ozone, PAN, and H_2O_2 are all secondary pollutants formed after an initial induction period, stations for monitoring peak concentrations should be located downwind of the urban center of precursor emissions.

The reactivity and instability of O_3 and other photochemical oxidants dictate special sampling techniques. Samples of air containing O_3 cannot be collected and stored and must be analyzed dynamically. Analysis for PAN must likewise be performed as soon as possible after collection. Hydrogen peroxide collected in aqueous media is fairly stable, but samples are subject to interfering reactions from ozone trapped in solution (section 5.5.8). Sampling probes should be constructed of Teflon or some similarly inert material, and inlet residence times should be as short as possible. Other design criteria for O_3 monitoring stations have been given (Standing Air Monitoring Work Group, 1977; National Academy of Sciences, 1977b). The most important of these are that inlets of the sampling probe should be positioned 3 to 15 m (10 to 49 ft) above ground and at least 4 m (13 ft) from large trees and 120 m (349 ft) from heavy automobile traffic.

5.6.4.2 Measurement Methods for Total Oxidants and Ozone. Techniques for the continuous monitoring of total oxidants and O_3 in ambient air are summarized in Table 5-13. The earliest methods used for routinely monitoring oxidants in the atmosphere were based on iodometry. When atmospheric oxidants are absorbed in potassium iodide (KI) reagent, the iodine produced,

$$O_3 + 3I^- + H_2O = I_3^- + O_2 + 2OH^- \qquad (5\text{-}85)$$

is measured by ultraviolet absorption in colorimetric instruments and by amperometric means in electrochemical instruments. The term "total oxidants" is of historical significance only and should not be construed to mean that such measurements yield a sum of the concentrations of the oxidants in the atmosphere. The various oxidants in the atmosphere react to yield iodine at different rates and with different stoichiometries. Only ozone reacts immediately to give a quantitative yield of iodine. Hydrogen peroxide, for example, produces iodine at a slow rate and because of its low concentration compared to ozone (see section 5.5.9) would be expected to have little effect upon a total oxidants measurement. As discussed below, the total oxidants measurement correlates fairly well with the specific measurement of ozone, except during periods when significant NO_2 and SO_2 interferences are present. The major problem with the total oxidants measurement was the effect of these interferences. Total oxidants instruments have now been replaced by specific ozone monitors in all aerometric networks and in most research laboratories. Biases among and between "total oxidants" and ozone methods are still important, however, for evaluating existing data on health and welfare "effects levels" where concentrations were measured by "total oxidants" methods.

The reference method promulgated by EPA for compliance monitoring is the chemiluminescence technique based on the gas-phase ozone-ethylene reaction (U.S. Environmental Protection Agency, 1971). The technique is specific for ozone, the response (luminescence intensity) is a linear function of concentration, detection limits of 0.001 to 0.005 ppm are readily obtained, and response times of 30 seconds or less are readily obtained. Prescribed methods of testing and prescribed performance specifications that a commercial analyzer must meet in order to be designated as a reference method or an equivalent method have been published by EPA (U.S. Environmental Protection Agency, 1975). An analyzer may be designated as a reference method if it is based on the same principle as the reference method and meets performance specifications. Commercial analyzers that have been designated as reference methods were listed in Table 5-8. An acceptable equivalent method must meet the prescribed performance specifications and also show a consistent relation with the reference method. Commercial analyzers that have been designated as equivalent methods were also listed in Table 5-8.

The designated equivalent methods are based on either the gas-solid chemiluminescence procedure or the ultraviolet absorption procedures (Table 5-14). The first designated equivalent method was based on ultraviolet absorption of the mercury 254 nm emission line. The absorption coefficient of ozone is accurately known at this wavelength with an accepted value of 134 M^{-1} cm^{-1}. Detection limits of 0.005 ppm are readily obtained by modern digital capabilities for making precise measurements of weak absorbancies at moderate pathlengths. Compensation for potential interferences that also absorb at 254 nm is made by comparing an averaged transmission signal of ozone in air to the transmission signal through an otherwise identical air sample from which the ozone has been preferentially scrubbed. Advantages of this UV absorption technique are that a reagent gas is not required and control of sample air flow is not critical. In addition, the measurement is in principle an absolute one, in that the ozone concentration can be computed from the measured transmission signal since the absorption coefficient and pathlength are accurately known.

In the gas-solid chemiluminescence analyzer, the reaction between ozone and Rhodamine-B adsorbed on activated silica produces chemiluminescence, the intensity of which is directly proportional to ozone concentration. The sensitivity is greater than the gas-phase chemiluminescence method and a controlled reagent gas flow is not required. The sensitivity of the reaction surface decays gradually with time, but the analyzer contains internal means to compensate for the decay.

TABLE 5-14. SUMMARY OF OZONE MONITORING TECHNIQUES

Principle	Reagent	Response	Minimum detection limit	Response time, 90% FS[a]	Major interferences	References
Continuous colorimetric	10(20)% KI buffered at pH = 6.8	Total oxidants	0.010 ppm	3 to 5 minutes	NO_2(+20%, 10%RI) SO_2(-100%)	Littman and Benoliel (1973) Tokiwa et al. (1972)
Continuous electrochemical	2% KI buffered at pH = 6.8	Total oxidants	0.010 ppm	1 minute	NO_2(+6%) SO_2(-100%)	Brewer and Milford (1960) Mast and Saunders (1962) Tokiwa et al. (1972)
Chemiluminescence	Ethylene, gas-phase	O_3-specific	0.005 ppm	< 30 seconds	None[b]	Nederbragt (1965) Stevens and Hodgeson (1973)
Chemiluminescence	Rhodamine-B	O_3-specific	0.001 ppm	< 1 minute	None	Regener (1960, 1964) Hodgeson et al. (1970)
Ultraviolet photometry	None	O_3-specific	0.005 ppm	30 seconds	Species that absorb at 254 nm[c]	Bowman and Horak (1974)

[a] FS = full response.

[b] A signal enhancement of 3 to 12% has been reported for measurement of O_3 in humid versus dry air (California Air Resources Board, 1976).

[c] No significant interferences have been reported in routine ambient air monitoring. If abnormally high concentrations of species that absorb at 254 nm (e.g., aromatic hydrocarbons and mercury vapor) are present, some positive response may be expected. If high aerosol concentrations are sampled, inlet filters must be used to avoid a positive response.

5.6.4.3 Calibration Methods. All the analyzers discussed above must be periodically calibrated with ozonized air streams, in which the ozone concentration has been determined by some absolute technique. This includes the UV absorption analyzer, which, when used for continuous ambient monitoring, may experience ozone losses in the inlet system because of contamination.

An ozone calibration system for a primary laboratory calibration system consists of a clean air source, an ozone generator, and a sampling manifold. The ozone generator most often used is a photolytic source employing a mercury pen-ray lamp that irradiates a quartz tube through which clean air flows at a controlled rate (Hodgeson et al., 1972b). The ozone concentration may be varied by means of a mechanical sleeve over the lamp envelope or by changing the lamp voltage or current. Once the output of the generator has been calibrated by a primary reference method, it may be used to calibrate O_3 transfer standards, which are portable generators, instruments, or other devices used to calibrate analyzers in the field. Reference calibration procedures that have been used for total oxidants and ozone-specific analyzers in this country are summarized in Table 5-15.

The original reference calibration procedure promulgated by EPA was the 1 percent neutral buffered potassium iodide (NBKI) method (U.S. Environmental Protection Agency, 1971). This technique was employed in most of the United States, with the exception of California, which routinely used a 2 percent NBKI procedure that was quite similar to the EPA method except for the use of humidified air through the ozone source (California Air Resources Board, 1976). The Los Angeles Air Pollution Control District (LAAPCD) used a 1 percent unbuffered KI procedure and measured the iodine produced by a titration technique rather than the photometric technique used in the California and EPA methods. A number of studies conducted between 1974 and 1978 revealed several deficiencies with KI methods, the most notable of which were poor precision or interlaboratory comparability and a positive bias of NBKI measurements relative to simultaneous absolute UV absorption measurements. The positive bias was also observed with respect to gas-phase titration (GPT) of ozone with standard nitric oxide (NO) samples. The positive bias observed is peculiar to the use of phosphate buffer in the NBKI techniques. The bias was not observed in the unbuffered LAAPCD method (which nevertheless suffered from poor precision), nor in the 1 percent EPA KI method without phosphate buffer (Hodgeson et al., 1977), nor in a KI procedure that used boric acid as buffer (Flamm, 1977). A summary

TABLE 5-15. OZONE CALIBRATION TECHNIQUES

Method	Reagent	Primary standard[a]	Method used, organization, and dates	Purpose	Bias, $[O_3]_i/[O_3]_{uv}$
1% NBKI	1% KI, phosphate buffer pH = 6.8	Reagent grade arsenious oxide	EPA 1971-1976	Primary reference procedure	1.12 ± 0.05[b]
2% NBKI	2% KI phosphate buffer pH = 6.8		CARB until 1975	Primary reference procedure	1.20 ± 0.05[b]
1% Unbuffered KI	1% KI pH = 7		LAAPCD until 1975	Primary reference procedure	0.96[c]
UV photometry	None	O_3 absorptivity at Hg 254 nm emission line	All 1979-present	Primary reference procedure[d]	
Gas-phase titration (GPT)	No standard reference gas	No SRM (50 ppm in N_2) from NBS	EPA, States 1973-present	Alternative reference procedure (1973-1979) Transfer standard (1979-present)	1.030 ± 0.015[e]
1% BAKI	1% KI, boric acid buffer pH = 5	Standard KIO_3[f] solutions	EPA 1975-1979	Alternative reference procedure	1.00 ± 0.05

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[a] In the case of the iodometric methods, the primary standard is the reagent used to prepare or standardize iodine solutions.

[b] The uncertainty limits represent the range of values obtained in several independent studies.

[c] Only one study available (Demore et al., 1976).

[d] UV photometry used as reference method by CARB since 1975. This technique used as an interim, alternative reference procedure by EPA from 1976 to 1979.

[e] This is the value reported in the latest definitive study (Fried and Hodgeson, 1982). Previous studies reported biases ranging from 0 to 10 percent (Burton et al., 1976; Paur et al., 1979).

[f] This procedure also recommended a standard I_3^- solution absorptivity to be used instead of the preparation of standard iodine solutions.

of results of these prior studies was presented in the previous criteria document (U.S. Environmental Protection Agency, 1978) and in a review by Burton et al. (1976). Correction factors for converting NBKI calibration data to a UV photometry basis were given in Table 5-5 and discussed in section 5.5.5.2.1.

Subsequently, EPA evaluated four alternative reference calibration procedures based on UV photometry, GPT with excess NO, GPT with excess ozone and the boric acid buffered KI technique (BAKI). The results of these studies (Rehme et al., 1981) showed that UV photometry was superior in accuracy, precision, and simplicity of use; and in 1979 regulations were amended to specify UV photometry as the reference calibration procedure (U.S. Environmental Protection Agency, 1979). Laboratory photometers used as reference systems for absolute O_3 measurements have been described by Demore and Patapoff (1976), Bass et al. (1977), and Paur and Bass (1983).

These laboratory photometers contain long path cells (1 to 5 m) and employ sophisticated digital techniques for making effective double beam measurements of small absorbancies and low ozone concentrations. A primary standard UV photometer, such as those above, is one that meets the requirements and specifications given in the revised ozone calibration procedures (U.S. Environmental Protection Agency, 1979). Since these are currently available in only a few laboratories, EPA has allowed the use of transfer standards, which are devices or methods that can be calibrated against a primary standard and transferred to another location for calibration of O_3 analyzers. Examples of transfer standards that have been used are commercial O_3 photometers, calibrated generators, and GPT apparatus. Guidelines on transfer standards have been published by EPA (McElroy, 1979).

5.6.4.4 Relationships of Total Oxidants and Ozone Measurements. The temporal and quantitative relationship between simultaneous total oxidants and ozone measurements has been examined in this chapter because of the existence of a data base obtained by "total oxidants" measurements. Such a comparison is complicated by the relative scarcity of data, the presence of both positive (NO_2) and negative (SO_2) interferences in total oxidants measurements, and the change in the basis of calibration. In particular, the presence of NO_2 and SO_2 interferences prevents the establishment of a definite quantitative relationship between ozone and oxidants data. Nevertheless, some interesting conclusions can be drawn and are summarized below.

An expected relationship between total oxidants and specific O_3 measurements can be predicted based upon the known response of oxidant instrumentation to oxidizing and reducing species in the atmosphere. The predicted relation in this document assumes that NO_2 is the only significant positive interference and that SO_2 is the predominant negative interference. Because of the potential presence of oxidizing (NO_2) and reducing (SO_2) interferences, it is difficult or impractical to intercompare measurements during evening and early morning hours when ozone concentrations are at a minimum. The relationship is best compared at the midday to early afternoon diurnal maximum of ozone when NO_2 concentrations are approaching a minimum; the SO_2 concentration at this time will depend on local emissions. A comparison of maximum hourly averages is appropriate since the primary and secondary ambient air quality standards are based on this value. If legitimate corrections or compensations have been made for SO_2 and NO_2 interferences, the corrected total oxidants concentrations should always be higher than simultaneous O_3 concentrations by an amount dependent on type and concentrations of other oxidants present. The major other oxidants known to exist in the atmosphere are PAN and H_2O_2. Maximum concentrations of these oxidants occur near the ozone diurnal maximum (chapter 6) with values that are only a fraction of the O_3 maximum (section 6.6 and 6.7). In addition, both of these are classified as slow oxidants in that they release iodine at a slow rate in aqueous solution. Therefore, if a contribution from these species is discernible at all in the total corrected oxidants reading, it should be only a small fraction of the ozone contribution. For most of the aerometric data base, particularly outside the state of California, no attempts were made to correct total oxidants concentrations for NO_2 and SO_2 because such corrections were impractical or impossible. For uncorrected total oxidants data, the counterbalancing effects of SO_2 and NO_2 interferences make it even more difficult to discern contributions from oxidants other than ozone. The uncorrected total oxidants data should then be either higher than or lower than corresponding ozone data, depending on the relative concentrations of SO_2 and NO_2.

The simultaneous comparisons that have been made in large part confirm the predictions above. Studies concluded in the early to mid-1970s were reviewed in the previous criteria document (U.S. Environmental Protection Agency, 1978). Averaged data showed fairly good qualitative and quantitative agreement between diurnal variations of total oxidants and ozone. Monthly averaged data from Los Angeles (Figure 5-4) and St. Louis (Figure 5-5) are illustrative. These uncorrected data show distinct morning and evening peaks resulting from NO_2 interference. Data taken from individual days of this study show considerably more variation, with total oxidants measurements both higher and lower than ozone measurements.

The most recent comparison in the literature involved simultaneous ozone and total oxidant measurements in the Los Angeles basin by the California Air Resources Board (1978) in 1974, 1976, and 1978. The maximum hourly data pairs were correlated (Chock et al., 1982) and yielded the following regression equation for 1978, in which a large number (927) of data pairs were available:

$$\text{Oxidant (ppm)} = 0.870\ O_3 + 0.005$$
$$\text{(Correlation coefficient} = 0.92) \qquad (5\text{-}86)$$

The oxidant data were uncorrected for NO_2 and SO_2 interferences, and, again, on individual days maximum oxidant averages were both higher than and lower than ozone averages.

In summary, specific ozone measurements agree fairly well with total oxidants corrected for NO_2 and SO_2 interferences, and in such corrected total oxidants measurements ozone is the dominant contributor to total oxidants. Indeed, it is difficult to discern the presence of other oxidants in most total oxidant data. There can, however, be major temporal discrepancies between ozone and oxidants data, which are primarily a result of oxidizing and reducing interferences with KI measurements. As a result of these interferences, on any given day the total oxidant values may be higher than or lower than simultaneous ozone data. The measurement of ozone is a more reliable indicator than total oxidant measurements of oxidant air quality.

5.6.4.5 Methods for Sampling and Analysis of Peroxyacetyl Nitrate and Its Homologues. Only two analytical techniques have been used to obtain significant data on ambient peroxyacetyl nitrate (PAN) concentrations. These are gas chromatography with electron capture detection (GC-ECD) and long-path Fourier transform infrared (FTIR) spectrometry. Atmospheric data on PAN concentrations have been obtained predominantly by GC-ECD because of its relative simplicity and superior sensitivity. These techniques have been described in this chapter along with attendant methods of sampling. Since PAN is thermodynamically unstable, standards must be generated and analyzed by some absolute technique for the purpose of calibrating the GC-ECD. Thus, PAN generation techniques and absolute methods for analyzing these samples have also been summarized.

By far the most widely used technique for the quantitative determination of ppb concentrations of PAN and its homologues is GC-ECD (Stephens, 1969). With carbowax or SE30 as a stationary phase, PAN, peroxypropionyl nitrate (PPN), peroxybenzoyl nitrate (PBzN), and other homologues (e.g., peroxybutyrl nitrate) are readily separated from components such as air, water, and other atmospheric compounds, as well as ethyl nitrate, methyl nitrate, and other contaminants that are present in synthetic mixtures. Electron-capture detection provides sensitivities in the ppb and sub-ppb ranges. Table 5-16 shows parameters used by several investigators to determine trace levels of PAN by GC-ECD. Sample injection into the GC is accomplished by means of a gas-sampling valve with a gas-sampling loop of a few milliliters' volume. Sample injection may be performed manually or automatically. Typically, manual air samples are collected in 50-200 ml ungreased glass syringes and purged through the gas-sampling valve. Samples collected from the atmosphere should be analyzed as soon as possible because PAN and its homologues undergo thermal decomposition in the gas phase and at the surface of containers.

The recent work of Singh and Salas (1983a, 1983b) on the measurement of PAN in the free (unpolluted) troposphere (see chapter 6) is illustrative of current capabilities for measuring low concentrations. A minimum detection limit of 0.010 ppb was obtained. The literature contains conflicting reports on the effects of variable relative humidity on PAN measurements by GC-ECD. Some investigators have reported a reduced response to PAN calibration samples when dry diluent gas is used, whereas others have not observed this effect. The reduced response has been attributed to losses of PAN to surfaces within the inlet system and the GC. Presumably, water vapor may deactivate surfaces. For the present, if a moisture effect is suspected in a PAN analysis, the bulk of this evidence suggests that humidification of PAN calibration samples (to a range approximating the humidity of the samples being analyzed) would be advisable.

Conventional long-path infrared spectroscopy and Fourier-transform infrared spectroscopy (FTIR) have been used to detect and measure atmospheric PAN. Sensitivity is enhanced by the use of FTIR. The most frequently used IR bands have been assigned and the absorptivities shown in Table 5-17 permit the quantitative analysis of PAN without calibration standards. The absorptivity of the

TABLE 5-16. SUMMARY OF PARAMETERS USED IN DETERMINATION OF PAN BY GC-ECD

Reference	Column dimensions and material	Stationary phase	Solid support	Column temperature, °C	Flow rate, ml/min	Carrier gas	Elution time, min	Concentration range
Heuss and Glasson, 1968	4 ft x 1/8 in Glass	SE30 (3.8%)	80-100 Mesh Diatoporte S	25	N.A.[a]	N.A.[a]	N.A.[a]	ppb range
Grosjean, 1983	6 ft x 1/8 in Teflon	10% Carbowax 400	60/80 Mesh Chromosorb P	30	40	N_2	N.A.[a]	ppb range
Darley et al., 1963	3 ft x 1/9 in Glass	5% Carbowax 400	100-200 Mesh Chromosorb W	35	25	N_2	2.17	3 to 5 ppb
Stephens and Price, 1973	1.5 ft. x 1/8 in Teflon	5% Carbowax E 400	Chromosorb G 80/100 mesh treated with dimethyl dichlorosilane	25	60	N_2	1.75	37 ppb
Lonneman et al., 1976	3 to 4 ft x 1/8 in Glass	10% Carbowax 600	Gas Chrom Z	25	70	95% Ar 5% CH_4	2.7	0.1 to 100 ppb
Holdren and Spicer, 1984	5 ft x 1/8 in Teflon	60/80 Mesh Carbowax 600	Gas Chrom Z	35	70	90% Ar 10% CH_4	3.00	ppb
Peake and Sandhu, 1983	3.3 ft x 1/8 in Glass	5% Carbowax 600	Chromosorb W	33	50	N_2	N.A.[a]	0.2 to 20 ppb
Singh and Salas, 1983	1.2 ft x 1/8 in Teflon	10% Carbowax 600	80/100 Mesh Supelcoport	33	30	95% AR 5% CH_4	N.A.[a]	0.02-0.10 ppb
Grosjean et al., 1984	1.7 ft x 1/8 in Teflon	10% Carbowax 400	60/80 Mesh Chromosorb G	30	40	N_2	5.0	2-400 ppb
Nielson et al., 1982	3.9 ft x 1/12 in Glass	5% Carbowax 400	Chromosorb W - AW - DCMS	25	40	N_2	6.0	11 ppb

[a] N.A. - not available in reference.

TABLE 5-17. INFRARED ABSORPTIVITIES OF PEROXYACETYL NITRATE

		Absorptivity, $ppm^{-1}\ m^{-1} \times 10^4$				
Frequency cm^{-1}	Mode	Liquid PAN (Bruckmann and Willner, 1983)	PAN in air (Stephens, 1969)	Frequency cm^{-1}	PAN in air (Stephens and Price, 1973)	PAN in octane (Holdren and Spicer, 1984)
1842	$\nu(c{=}o)$	12.4	10.0	1830	10.0	9.44
1741	$\nu_{as}(NO_2)$	32.6	23.6	1728	23.6	26.5
1302	$\nu_s(NO_2)$	13.6	11.2	1294	11.4	9.44
1162.5	$\nu(c{-}o)$	15.8	14.3	1153	13.9	9.66
930	$\nu(o{-}o)$	N.A.[a]	N.A.[a]	930	1.8	N.A.[a]
791.5	$\delta(NO_2)$	13.4	10.1	787	10.3	10.1

[a] Not available in reference.

990 cm^{-1} band of PBzN has been reported by Stephens (1969). Some recent simultaneous measurements of PAN and other atmospheric pollutants such as O_3, HNO_3, HCOOH, and HCHO have been made by long-path FTIR spectrometry during smog episodes in the Los Angeles Basin. Tuazon et al. (1978) describes an FTIR system operable at pathlengths up to 2 km for ambient measurements of PAN and other trace constituents. This system employed an eight-mirror multiple reflection cell with a 22.5-m base path. Detection of PAN was by bands at 793 and 1162 cm^{-1}. The 793 cm^{-1} band is characteristic of peroxynitrates, while the 1162 cm^{-1} band is reportedly attributable to PAN only (Hanst et al., 1982). Tuazon et al. (1981) reported a detection limit for PAN of 3 ppb at a 900-meter pathlength.

Hanst et al. (1982) made measurements with a 1260-m folded optical path system during a 2-day smog episode in Los Angeles in 1980. An upper limit of 1 ppb of peroxybenzoyl nitrate (PbzN) was placed, based on observations in the vicinity of the PBzN band at 990 cm^{-1}; the maximum PAN concentration observed was 15 ppb.

Sampling may constitute one of the major problems in the analysis of trace reactive species, such as PAN, by long-path FTIR spectrometry. The large internal surface area of the White cells may serve to promote the decomposition or irreversible adsorption of reactive trace species. High volume sampling rates and inert internal surface materials are used to minimize these effects.

Because of the thermal instability of dilute PAN samples and the explosive nature of purified PAN, calibration samples are not commercially available. Each laboratory involved in making such measurements must prepare its own standards. Calibration samples are usually prepared by various means at concentrations in the ppm range, and they must be analyzed by some absolute technique.

Earlier methods used to synthesize PAN have been summarized by Stephens (1969). The photolysis of alkyl nitrites in oxygen was the most commonly used procedure and may still be used by some investigators. As described by Stephens et al. (1965), the liquefied crude mixture obtained at the outlet of the photolysis chamber is purified by preparation-scale GC. [CAUTION: Both the liquid crude mixture and the purified PAN samples are violently explosive and should be handled behind explosion shields using plastic full-face protection, gloves, and a leather coat at all times.] The pure PAN is usually diluted to about 1000 ppm in nitrogen cylinders at 100 psig and stored at reduced temperatures, <15°C.

Gay et al. (1976) have used the photolysis of Cl_2:aldehyde:NO_2 mixtures in air or oxygen for the preparation of PAN and a number of its homologues at high yields. This procedure has been utilized in a portable PAN generator that can be used for the calibration of GC-ECD instruments in the field (Grosjean, 1983; Grosjean et al., 1984).

The other technique for PAN preparation in current use involves the nitration of peracetic acid. Several investigators have recently reported on a condensed-phase synthesis of PAN with peracetic acid that produces high yields of a pure product free of other alkyl nitrates (Hendry and Kenley, 1977; Kravetz et al., 1980; Nielsen et al., 1982; Holdren and Spicer, 1984). Most of these procedures call for the addition of peracetic acid (40 percent in acetic acid) to a hydrocarbon solvent (pentane, heptane, octane) maintained at 0°C in a dry-ice acetone bath, followed by acidification with sulfuric acid and slow addition of sodium nitrate. After the nitration is complete, the hydrocarbon fraction containing PAN concentrations of 2 to 4 mg/ml can be stored at -20°C for periods longer than a year (Holdren and Spicer, 1984).

The most direct method for absolute analysis of these PAN samples is by infrared absorption, using absorptivities given in Table 5-17. Conventional IR instruments and 10-cm gas cells can analyze gas standards of concentrations >35 ppm. Liquid microcells can be used for the analysis of PAN in octane solutions.

The alkaline hydrolysis of PAN to acetate ion and nitrite ion in quantitative yield (Nicksic et al., 1967) provides a means independent of infrared for the quantitative analysis of PAN. Following hydrolysis, nitrite ion may be quantitatively analyzed by the Saltzman colorimetric procedure (Stephens, 1969). The favored procedures now use ion chromatography to analyze for nitrite (Nielsen et al., 1982) or acetate (Grosjean, 1983, 1984) ions. Another calibration procedure has been proposed that is based on the thermal decomposition of PAN in the presence of excess NO (Lonneman et al., 1982; Lonneman and Bufalini, 1982). The peroxyradical, $CH_3C(O)O_2$, and its decomposition products rapidly oxidize NO to NO_2 with a stoichiometry that has been experimentally measured. By the use of NO standard mixtures and the measurement by chemiluminescence of the NO consumed, the absolute PAN concentration can be determined.

5.6.4.6 Methods for Sampling and Analysis of Hydrogen Peroxide. Hydrogen peroxide (H_2O_2), like ozone and PAN, is formed as a product of the photooxidation of hydrocarbons and reaches maximum concentrations during daylight hours. There are some early reports of H_2O_2 concentrations as high as 180 ppb at an ozone maximum of 650 ppb, but it now appears more likely that maximum H_2O_2 concentrations are in the range of 10 to 50 ppb and are only a small fraction (< 10%) of the corresponding ozone maximum. Applied and potentially useful techniques for the measurement of ambient H_2O_2 are summarized in Table 5-18.

With the exception of Fourier-transform infrared (FTIR) studies, all of the techniques that have been used for atmospheric H_2O_2 measurements have employed aqueous traps for sampling. Recent studies have indicated that this approach leads to interference from ozone, which will always be present at higher concentrations. Absorbed O_3 has been observed to promote both the formation and destruction of H_2O_2 in aqueous media (Zika and Saltzman, 1982). Therefore, an obvious research need in H_2O_2 measurements is a clear delineation of the nature of any O_3 interferences and the development of means for their prevention.

Of the procedures given in Table 5-18, only the titanium colorimetric, enzyme-catalyzed, and FTIR methods have been used for atmospheric sampling. The other procedures do not appear promising for ambient air analysis. The titanium sulfate-8-quinolinol reagent has been used in several earlier studies on atmospheric H_2O_2 (Bufalini et al., 1972; Gay et al., 1972a; Gay et al., 1972b; Kok et al., 1978a). Hydrogen peroxide in air is scrubbed in a coarse-fritted bubbler containing aqueous titanium sulfate-ammonium sulfate-sulfuric acid solution. After sampling, the solution is extracted with an aliquot of 8-quinolinol in chloroform. The absorbance at 450 nm of the titanium (IV)-H_2O_2-9-quinolinol complex in chloroform is determined. A positive interference is expected from any compound that can liberate H_2O_2 via acid hydrolysis (Pobiner, 1961), e.g., t-butylhydroperoxide. Of the major atmospheric pollutants investigated (SO_2, O_3, NO_2, NO, and hydrocarbons), only SO_2 at high concentrations gave a small (0.7 percent) negative interference (Gay et al., 1972b).

In the titanium tetrachloride method, samples are collected in a midget impinger containing an aqueous $TiCl_4$-HCl solution. A stable $TiCl_4$-H_2O_2 complex is formed immediately, and after the solution is diluted to a known volume, the absorbance of the complex at 410 nm is determined. The principal difficulty with this method is the formation of fine particles, presumably TiO_2, which scatter visible radiation and create an apparent absorption. In an intercomparison of H_2O_2 measurement methods, Kok et al. (1978a) reported rather poor agreement between the two titanium reagents and between these and chemiluminescence.

TABLE 5-18. MEASUREMENT METHODS FOR HYDROGEN PEROXIDE

Method	Reagent(s)	Limits of detection[a]	Interferences[b]		Applications	Primary reference
			Positive	Negative		
Titanium colorimetry	(1) Titanium Sulfate -8-Quinolinol (2) Titanium Tetrachloride	(1) 1.6 x 10^{-6} M (2) ca 10^{-6} M	Alkyl hydroperoxides	SO_2[c]?	Atmospheric	(1) Gay et al. (1972a, 1972b) (2) Pilz and Johann (1974); Kok et al. (1978a)
Chemiluminescence	Luminol, Cu(II) basic solution	0.001 to 1 ppm	PAN[d]	SO_2[e]	Atmospheric, rainwater	Armstrong and Humphreys (1965); Kok et al. (1978a,1978b)
Enzyme-catalyzed	Scopoletin, horseradish-peroxidase (HRP)	1.5 x 10^{-11} M	NA	NA	Atmospheric, rainwater	Andreae (1966); Perschke and Broda (1961); Zika and Saltzman (1982)
Enzyme-catalyzed	Leuco crystal violet, HRP	10^{-8} M	NA	NA	---	Mottola et al. (1970)
Enzyme-catalyzed	3-(p-hydroxyphenyl) propionic acid	10^{-6} to 10^{-4} M[f]	NA	NA	---	Zaitsu and Ohkura (1980)
Fourier-transform infrared absorption	None	0.005 ppm (est.)	NA[g]	None	Atmospheric[h]	Hanst et al. (1982)
Electrochemical	Aqueous solutions	5 x 10^{-6} to 1 M	NA	NA	---	Pisarevskii and Polozova (1980)
H_2O_2-olefin reactions	1,2-di-(4-pyridyl) ethylene	10^{-6} to 5 x 10^{-4} M	O_3	NA	---	Hauser and Kolar (1968)
Mixed-ligand complex reagents	Vanadium and uranium hydroxamic acid chelates	10^{-6} M	NA	NA	---	Csanyi (1981); Meloan (1961)

[a] Except where noted, detection limits are in moles/liter(M) in aqueous solution.

[b] O_3 may be both a positive and negative interference in all these procedures using aqueous sampling. See Text. NA = not available.

[c] The SO_2 interferences is reported to be small at high SO_2 concentrations (Gay et al., 1972b). Studies of potential positive and negative interferences are incomplete for these methods.

[d] The reported PAN interference is small (Kok et al., 1978b).

[e] The report of an SO_2 interference is undocumented.

[f] The lower limit could presumably be reduced by the use of larger samples.

[g] With sufficient resolution, there should be no interferences. IR absorption by atmospheric water vapor is the major analytical limitation.

[h] H_2O_2 bands have not been observed in any long-path FTIR studies. The estimated lower limit of detection in these studies is approximately 0.005 ppm.

A promising method for the measurement of hydrogen peroxide in the atmosphere at very low concentrations is based on the chemiluminescence obtained from the Cu(II)-catalyzed oxidation of luminol (5-amino-2,3 dihydro-1,4-phthalazinedione) by H_2O_2 (Armstrong and Humphreys, 1965). The product of the reaction with H_2O_2 is 3-amino-phthalic acid, a nitrogen molecule, and a photon of light at 450 nm. A small positive interference was reported for PAN (Kok et al., 1978b). If O_3 absorption leads to the formation of H_2O_2 as reported (Zika, 1982; Heikes et al., 1982), then O_3 is a major interference. There have also been undocumented reports of a negative interference from SO_2.

Perhaps the most promising chemical approach for the measurement of trace concentrations of H_2O_2 employs the catalytic acitivity of the enzyme, horseradish peroxidase (HRP), on the oxidation of organic substrates by H_2O_2. This general method involves three components: a substrate that is oxidizable, HRP, and H_2O_2. Three substrates that have been used are scopoletin (6-methoxy-7-hydroxy-1,2-benzopyrone), 3-(p-hydroxyphenyl)propionic acid (HPPA), and leuco crystal violet (LCV). The scopoletin reagent has recently been used in atmospheric analysis. The disappearance of scopoletin fluorescence, upon oxidation of scopoletin by H_2O_2, is monitored and the fluorescence intensity is used to obtain the concentration of H_2O_2 from a calibration curve. The most significant advantage of the scopoletin method is the sensitivity (ca. 16^{-11} M). The chief disadvantage of the method is that the concentration of H_2O_2 must be within a narrow concentration range in order to obtain an accurately measurable decrease in fluorescence. This limits the usefulness of the technique in determining unknown H_2O_2 concentrations over several orders of magnitude. With the leuco crystal violet (LCV) substrate, intensely colored crystal violet is formed from the reaction of H_2O_2 with LCV, catalyzed by HRP. The absorbance is measured at 596 nm, where the molar absorption coefficient of crystal violet is 10^5 M^{-1} cm^{-1}, a very high value and an inherent advantage of this method. Finally, Zaitsu and Ohkura (1980) have tested a number of 4-hydroxy phenyl compounds and found that 3-(p-hydroxyphenyl) propionic acid (HPPA) provided a sensitive and rapid means for determining H_2O_2. A product is formed that fluoresces at 404 nm, and the intensity of this fluorescence is monitored as a function of H_2O_2 concentration. The detection limit was reported to be 10^{-10} mole H_2O_2 with a test solution of only 0.1 ml volume used. The molar sensitivity could presumably be improved by the use of large sample volumes.

The enzymatic methods appear to be the most promising colorimetric methods of H_2O_2 and have considerably greater sensitivity than the methods employing titanium reagents. However, studies of potential atmospheric interferences have apparently not been conducted for any of these three substrates.

Hydrogen peroxide can be monitored directly in the gas phase by FTIR absorption at 1250 cm^{-1}, where the absorption coefficient is 8.4 cm^{-1} atm^{-1} at 1 cm resolution (Hanst et al., 1981). One FTIR measurement of the possible presence of 0.070 ppm H_2O_2 was reported during an intense smog episode in Pasadena, California (Hanst et al., 1975). Unfortunately, minimum detection limits at 1 km pathlength are degraded to 0.040 ppm because of neighboring absorption bands of H_2O and CH_4 (Hanst et al., 1981).

As with O_3, H_2O_2 calibration standards are not commercially available and are usually prepared at the time of use. The most convenient method for preparing aqueous samples containing micromolar concentrations of H_2O_2 is simply the serial dilution of commercial grade 30 percent H_2O_2 (Fisher Analytical Reagent). Techniques for the convenient generation of gas-phase standards are not available. A technique often used for generating ppm concentrations of H_2O_2 in air involves the injection of microliter quantities of 30 percent H_2O_2 in air involves the injection of microliter quantities of 30 percent H_2O_2 solution into a metered stream of air that flows into a Teflon bag. Aqueous and gas-phase samples are then standardized by conventional iodometric procedures (Allen et al., 1952; Cohen et al., 1967).

Hydrogen peroxide liberates iodine from an iodide solution quite slowly, but in the presence of a molybdate catalyst the reaction is rapid. The iodine liberated can be determined by titration with standard thiosulfate at higher concentrations or by photometric measurement of the tri-iodide ion at low concentrations. The molar absorption coefficient of the tri-iodide ion at 350 nm has been determined to be 2.44 x 10^4 (Armstrong and Humphreys, 1965). The stoichiometry is apparently 1 mole of iodine released per mole of H_2O_2. However, definitive studies of the stoichiometry have not been performed for H_2O_2 as they have for the iodometric determination of O_3.

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6. CONCENTRATIONS OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS IN AMBIENT AIR

6.1 INTRODUCTION

The data presented in this chapter on the concentrations of ozone and other photochemical oxidants in ambient air are intended to support and complement information presented in subsequent chapters on the effects of these compounds. Thus, this chapter describes potential exposures of human populations, crops, ecosystems, and nonbiological materials in general terms for the entire nation and in specific terms for selected areas of the country. Since the health and welfare effects of ozone have been much more thoroughly documented than those of other related oxidants, primary emphasis in this section has been placed on the concentrations of ozone found in ambient air. Potential exposures are described by presenting data on peak (or second-highest) and average concentrations nationwide and on seasonal and diurnal patterns in selected urban and nonurban areas. The patterns of sustained or recurring concentrations of respective incremental levels of ozone have been examined for selected sites in order to aid in understanding the significance of health and welfare effects documented in subsequent chapters. Likewise, data have been included that portray representative urban and rural concentrations by season and by time of day. In addition, data are presented on ozone or total oxidant concentrations that are relevant to epidemiological studies (chapter 12). Spatial variations in ozone concentrations are briefly addressed since latitude, altitude, and indoor-outdoor gradients are pertinent to the assessment of potential exposures of human populations, and except for the indoor-outdoor gradients, of crops and ecosystems.

Ozone is the only photochemical oxidant, other than nitrogen dioxide, that is routinely monitored and for which a comprehensive aerometric data base exists. Data for peroxyacetyl nitrate (PAN) and its homologues and for hydrogen peroxide (H_2O_2) and formic acid (HCOOH) have all been obtained as part of special research investigations. Consequently, no nationwide patterns are available for these oxidants, nor are data available that would permit the extensive examination of the occurrence of these oxidants or of the correlations of levels and patterns of these oxidants with those of ozone. Sections 6.6 and 6.7 present, however, a reasonably extensive review of concentration data for these other oxidants.

As documented in the discussions that follow, the occurrence in ambient air of ozone at concentrations above 0.12 ppm is both widespread and persistent in many areas of the country. High concentrations (i.e., above 0.12 ppm) may occur not only as single 1-hour exposures but also as recurring or sustained high levels that are present for several hours on any one day, and which, because of the persistence of meteorological patterns, are often repeated on consecutive days.

The concentrations of ozone and related photochemical oxidants observed in ambient air are the net result, as shown in the preceding chapter, of a combination of any or all of a variety of atmospheric processes, including:

1. Local photochemical production from oxides of nitrogen and reactive volatile organic compounds.
2. Transport of ozone produced photochemically but not locally.
3. Intrusion into the troposphere, even to ground level, of ozone-rich air from a ubiquitous stratospheric reservoir.
4. Formation of ozone photochemically in the mid-troposphere, with subsequent intrusion into the boundary layer.
5. Chemical scavenging in the atmosphere of ozone and other oxidants; e.g., the reaction of ozone with nitric oxide (NO) or the reaction of H_2O_2 with sulfur dioxide (SO_2).
6. Physical scavenging in the atmosphere of ozone and other oxidants; e.g., the temperature-dependent decomposition of PAN, the precipitation scavenging of H_2O_2, and the photolytic dissociation of ozone.
7. Combined physical and chemical scavenging processes at the earth's surface; e.g., the deposition of ozone on reactive biological or nonbiological surfaces, such as vegetation, soils, or certain polymers.

These processes include, obviously, both manmade and natural processes and driving mechanisms. Although the occurrence of high ozone concentrations is most commonly associated with recognized meteorological conditions that involve intense sunlight and elevated temperatures, the variety of processes that may be involved contribute to strong diurnal cycles, but peak concentrations have been observed to occur at almost any time of day. Ozone may be transported after its formation for distances up to 1000 km or more. Likewise, PAN and other oxidants can be transported long distances. As a result, high concentrations of ozone and related oxidants occur not only near large sources of precursors but also in downwind nonurban areas. Ozone, and apparently PAN, as well, can be transported at night above the surface pollutant and nocturnal inversion layer (chapter 4). Thus, low morning concentrations of ozone are no measure of the potential for high concentrations later in the day because downward mixing from the transported ozone reservoir aloft will occur. During daylight hours, ozone can be transported considerable distances at or near ground level.

The analysis of quantitative apportionment of observed concentrations between manmade and natural sources is germane primarily to understanding how stringent the control of controllable (manmade) sources must be and to formulating control strategies for attaining promulgated standards. Consequently, the emphasis of this chapter is on documentation of concentrations rather than on explanations of possible causes of observed concentrations. Probable causes and explanations are mentioned where they are pertinent to the discussion.

Most of the data presented in this chapter to characterize both nationwide and site-specific ozone concentrations in ambient air were obtained after 1978, although some older data are cited for purposes of historical and general comparisons. Two factors influenced the use of post-1978 data. First, the current Federal Reference Method for ozone, chemiluminescence, and the equivalent UV method were almost universally employed by 1979. Second, EPA promulgated a UV calibration method for ozone in 1979. Thus, these data form a relatively homogeneous set for purposes of intercomparison. Because of the well-recognized difficulties in converting from older data sets to the current reference method, the chief pre-1979 aerometric data for ozone presented in this section are those for specific sites and specific years that provide some background information for epidemiologic studies (chapter 12). In addition, some historical data on trends in ozone concentrations are given to help put more recent data in perspective.

6.2 HISTORICAL DATA ON OZONE/OXIDANT CONCENTRATIONS AND TRENDS IN AMBIENT AIR

6.2.1 Summary of Urban Oxidant Data, 1964 through 1975

Aerometric data published in the 1970 and 1978 criteria documents for ozone and other photochemical oxidants help provide perspective on the extent of the photochemical oxidant problem in the United States over a decade or more. Table 6-1, reproduced from the 1970 document, shows the maximum 1-hour-average oxidant concentration, the peak concentration (less than 1-hour averaging time), and the number and percentage of days on which the maximum 1-hour-average oxidant concentration exceeded the specified values. Data in this table were obtained from one site per city (U.S. Department of Health, Education, and Welfare, 1970). The measurements were made using potassium iodide total oxidants methods (chapter 5). As this table indicates, in the mid-1960s the percentage of days on which oxidant concentrations exceeded 0.15 ppm in Los Angeles and Pasadena, California, was an order of magnitude greater than in other cities both within California and in other locations where monitoring was carried out. In addition, during this 1964-1967 monitoring period the maximum hourly average observed in Pasadena, Los Angeles, and San Diego was typically twice that recorded elsewhere.

Table 6-2 shows the range of second-highest 1-hour-average concentrations (potassium iodide methods) in selected major cities in 1974 and 1975 (U.S. Environmental Protection Agency, 1978). This table, although tabulated in a different manner than Table 6-1, shows that for comparable cities there was no apparent increase in maximum concentrations between the 1964-1967 and 1974-1975 periods. The data are a gross indication of trends, but should not be overinterpreted, since the data may not have been obtained from the same sites or from the same number of observations.

6.2.2 Summary of Rural and Remote Ozone Data, 1957 through 1975

The 1978 criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1978) pointed out clearly that the ozone concentrations observed at nonurban sites could be the result of either transported manmade pollutants or naturally generated ozone, or combinations of both. Thus, it is not possible to categorize nonurban sites arbitrarily as being indicative of the natural atmospheric background; in fact, many rural areas can be shown to be strongly affected by upwind urban pollutant sources.

Historical data on "remote" or "rural" or "nonurban" ozone/oxidant concentrations have been taken from the 1970 and 1978 criteria documents and are shown in Tables 6-3, 6-4, and 6-5. The locations in Tables 6-3 and 6-4 are a mixture of obviously remote locations, such as Antarctica and Mauna Loa; and rural central continental locations that may or may not be immune from urban transport problems, such as Pocahontas County, West Virginia, and Arosa,

TABLE 6-1. SUMMARY OF MAXIMUM OXIDANT CONCENTRATIONS RECORDED IN SELECTED CITIES, 1964-1967

Station	Total days of available data	Total days with maximum hourly average equal to or greater than concentration specified						Maximum hourly average, ppm
		0.15 ppm		0.10 ppm		0.05 ppm		
		No. days	Percent of days	No. days	Percent of days	No. days	Percent of days	
Pasadena	728	299	41.1	401	55.1	546	75.0	0.46
Los Angeles	730	220	30.1	354	48.5	540	74.0	0.58
San Diego	623	35	5.6	130	20.9	540	74.0	0.58
Denver[a]	285	14	4.9	51	17.9	226	79.3	0.25
St. Louis	582	14	2.4	59	10.1	362	62.2	0.35
Philadelphia	556	13	2.3	60	10.9	233	41.9	0.21
Sacramento	711	16	2.3	104	14.6	443	62.3	0.26
Cincinnati	613	10	1.6	55	9.0	319	52.0	0.26
Santa Barbara	723	11	1.5	76	10.5	510	70.5	0.25
Washington, D.C.	577	7	1.2	65	11.3	313	54.2	0.21
San Francisco	647	6	0.9	29	4.5	185	28.6	0.18
Chicago	530	0	0	24	4.5	269	50.8	0.13

[a] 11 months of data beginning February 1965.

Source: U.S. Department of Health, Education, and Welfare, 1970.

TABLE 6-2. OXIDANT CONCENTRATIONS OBSERVED IN SELECTED URBAN AREAS OF THE UNITED STATES, 1974-1975

Urban areas	Total no. of valid sites	Range of second-highest 1-hr values µg/m^3	ppm
New York, NY - Northeastern NJ	8	259-510	0.13-0.26
Los Angeles - Long Beach, CA	3	255-784	0.13-0.40
Chicago, IL - Northwestern IN	6	163-427	0.08-0.22
Philadelphia, PA	10	216-625	0.11-0.32
Detroit, MI	2	455-514	0.23-0.26
Boston, MA	7	186-376	0.09-0.19
Washington, DC	8	363-451	0.18-0.23
Cleveland, OH	5	245-411	0.12-0.21
Minneapolis - St. Paul, MN	2	141-206	0.07-0.10
Houston - Galveston, TX	4	304-588	0.16-0.30
Baltimore, MD	2	314-372	0.16-0.19
Dallas - Fort Worth, TX	2	274-323	0.14-0.16
Milwaukee - Racine, WI	7	332-425	0.17-0.22
Seattle - Tacoma, WA	4	118-235	0.06-0.12
Cincinnati, OH - Northern KY	6	284-412	0.14-0.21
Denver, CO	6	212-349	0.11-0.18

[a] Only sites having a minimum of 4000 observations were included in this summary.

Source: U.S. Environmental Protection Agency, 1978.

TABLE 6-3. SUMMARY OF OXIDANT CONCENTRATIONS IN AMBIENT AIR AT RURAL AND REMOTE SITES, 1957 THROUGH 1967

Location	Period	Concentrations and averaging times	Reference
Greenland	July 1960	25 μg/m³ (0.013 ppm); instantaneous maximum	McKee (1961)
Antarctica	April 1957 through May 1958	20 to 67 μg/m³ (0.01 to 0.034 ppm); mean monthly avg. at surface	Odishaw (1959)
Geographic South Pole	1961 through 1964	40 to 80 μg/m³ (0.02 to 0.04 ppm); monthly mean, Regener method	Aldaz (1967)
	1963 and 1964	20 to 60 μg/m³ (0.01 to 0.03 ppm); monthly mean, Mast meter	
Petawawa Forest, Chalk River, Ontario	1967	~20 to ~80 μg/m³ (~0.01 to ~0.04 ppm), 15-min measurements (n = 6865), 24 hr/day	Canada, Dept. of Forestry and Rural Development (1967)
		mean of 22 μg/m³ (0.011 ppm) and maximum 15-minute of 120 μg/m³ (0.06 ppm)	
Greenknob, North Carolina	June 15, 1962-July 11, 1962	33 μg/m³ (0.017 ppm), mean conc; 140 μg/m³ (0.07 ppm), maximum instantaneous measurement (n = 2394)	U.S. Dept. of Interior, Southeastern Forest Exp. Station (1967)

TABLE 6-3. SUMMARY OF OXIDANT CONCENTRATIONS IN AMBIENT AIR AT RURAL AND REMOTE SITES, 1957 THROUGH 1967 (continued)

Location	Period	Concentrations and averaging times	Reference
Pocahontas County, West Virginia	June 6, 1961- July 6, 1961	49 μg/m³ (0.025 ppm), mean conc; 125 μg/m³ (0.064 ppm), maximum instantaneous measurement (n = 2880)	U.S Dept. of Interior, Southeastern Forest Exp. Station (1967)
Remote ground-level sites	-	20 to 60 μg/m³ (0.01 to 0.03 ppm), instantaneous measurements	Junge (1963)

Source: Tabulated from data in U.S. Department of Health, Education, and Welfare (1970).

TABLE 6-4. CONCENTRATIONS OF TROPOSPHERIC OZONE BEFORE 1962

References	Location, time, and remarks	Altitude[a]	O_3, μg/m³ Range[b]	O_3, μg/m³ Average[b]	O_3, ppb Range[b]	O_3, ppb Average[b]
Cötz and Volz (1951)	Arosa, Switzerland 1950-1957, high valley; daily maximum values.	1860 m	19-90	50	9.7-45.9	25.5
Regener (1957)	Mt. Capilio and Albuquerque,	3100 m	18-85	45	9.2-43.4	23.0
	New Mexico, 1951-1952.	1600 m	3-120	36	1.5-61.2	18.4
Regener (1957)	O'Neil, Nebraska, 1953.	12.5 m above ground	30-100	60	15.3-51.0	30.6
Ehmert (1952)	Weissenau, Bodensee, Germany, 1952.	20 m	0-90	36	0-45.9	18.4
		above ground	0-70	30	0-35.7	15.3
Teichert (1955)	Lindenberg, Obs., Germany, 1953-1954.	80 m	0-50	30	0-25.5	15.3
		above ground	0-50	27	0-25.5	13.8
Kay (1953)	Farnborough, England, 1952-1953.	0-12,000 m	26-50	36	13.3-25.5	18.4
Brewer (1955)	Tromsö, Norway 1954.	0-10,000 m	60-70	65	30.6-35.7	33.2
Rice and Pales (1959)	Mauna Loa Observatory, Hawaii.	3000 m	30-62	45	15.3-31.6	23.0
Wexler et al. (1960)	Little American Station, Antarctica.	100 m	20-60	45	10.2-30.6	23.0

[a] Above mean sea level, except as noted.

[b] As interpreted from the published data. The values sometimes represent absolute maxima, sometimes mean maxima.

Source: U.S. Environmental Protection Agency, 1978.

TABLE 6-5. SUMMARY OF OZONE DATA FROM RESEARCH TRIANGLE INSTITUTE STUDIES, 1973 THROUGH 1975

Station	Year	Station	Average ppm	Average μg/m^3	No. of hours $\geq$0.08 ppm	Total hours	% Hours ppm $\geq$ 0.08
McHenry, MD	1973	Rural	0.074	145	600	1662	37.0
Kane, PA	1973	Rural	0.065	127	639	2131	30.0
Coshocton, OH	1973	Rural	0.056	110	357	1785	20.0
Lewisburg, W VA	1973	Rural	0.052	187	249	1663	15.0
Wilmington, OH	1974	Rural	0.052	102	259	1751	14.9
McConnelsville, OH	1974	Rural	0.057	112	262	2011	13.0
Wooster, OH	1974	Rural	0.047	92	262	1878	14.0
McHenry, MD	1974	Rural	0.057	112	262	2011	13.0
DuBois, PA	1974	Rural	0.056	110	341	1667	20.5
Bradford, PA	1975	Rural	0.040	78	100	2332	4.3
Lewisburg, W VA	1975	Rural	0.038	74	59	2386	2.5
Creston, IA	1975	Rural	0.035	69	17	2117	0.8
Wolf Point, MT	1975	Rural	0.028	55	0	2160	0.0
De Ridder, LA	1975	Rural	0.030	59	38	2994	1.3
Poynette, WI	1975	Rural	0.038	74	126	2663	4.7
Port O'Conner, TX	1975	Rural	0.027	53	99	2912	3.4

Source: U.S. Environmental Protection Agency, 1978, modified.

Switzerland. On the basis, however, of the rather extensive studies that have been made of both nonurban and background ozone concentrations since the 1978 document, the patterns of maximum observed concentrations at these various sites are not outside the range of those that could occur as a result of natural ozone sources.

In contrast to Tables 6-3 and 6-4, Table 6-5 shows a number of examples of sites in rural areas where ozone concentrations clearly seem to be influenced by manmade pollutants. Examples of probable manmade influences are seen in the 1973 data from McHenry, Maryland, and Kane, Pennsylvania, where 30 percent or more of the samples over a 2- to 3-month period equalled or exceeded 0.08 ppm, a value that had not been equalled in the older and more remote sampling data. Wolf Point, Montana, data from 1975, as listed in Table 6-5, show results that are more characteristic of true natural background concentrations, based on the previous tabulations. All, however, of the data shown in Table 6-5 for 1975 from this Research Triangle Institute research program are much lower than the data from earlier years. Whether this is because of the sampling period selected, relevant weather factors, measurement calibration biases, or a combination of these, is unknown.

Thus, as stated above, ozone/oxidant data from a variety of rural and more remote nonurban sites show that these locations may experience a wide variety of ozone concentration patterns. The assumption that a nonurban site will be exposed only to natural or background atmospheric ozone concentrations cannot be made. This point will be discussed in more detail in a later section when newer research is introduced.

6.2.3 Seasonal and Diurnal Variations in Ozone or Oxidants Prior to 1970

Seasonal variations in tropospheric ozone concentrations have been observed for many years. In the absence of anthropogenic influences peak concentrations most frequently occurred in the spring months and were attributed to the influence of seasonal changes in both the stratospheric source and vertical transport mechanisms. Figures 6-1 and 6-2 show the average monthly ozone concentrations at Quillayute, Washington, a sea-level coastal station; and Mauna Loa, Hawaii, a mountain observatory 11,300 ft above MSL. Although data for only 2 years or less are shown in these figures, a springtime relative maximum is discernable, especially in the data from the higher-altitude station at Mauna Loa.

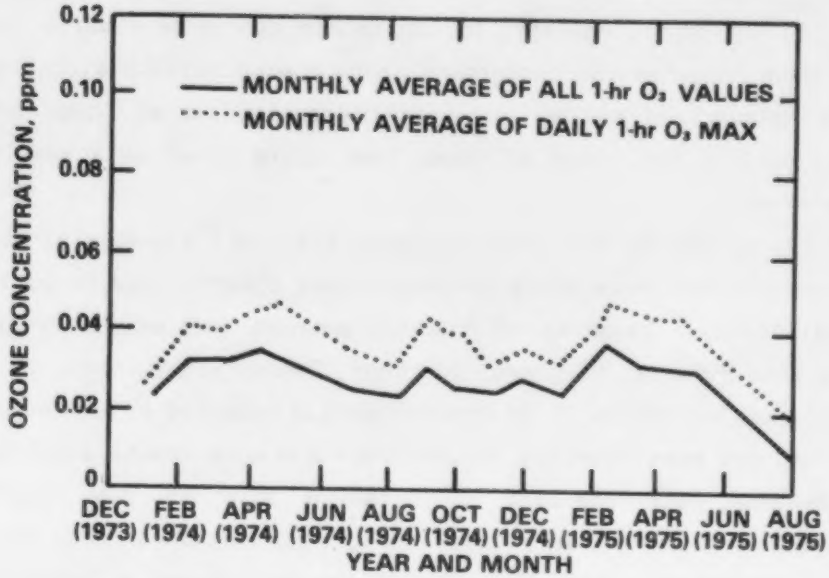


Figure 6-1. Long-term monthly ozone variations at Quillayute, Washington.

Source: Derived from Singh et al. (1977); cited in U.S. Environmental Protection Agency (1978)

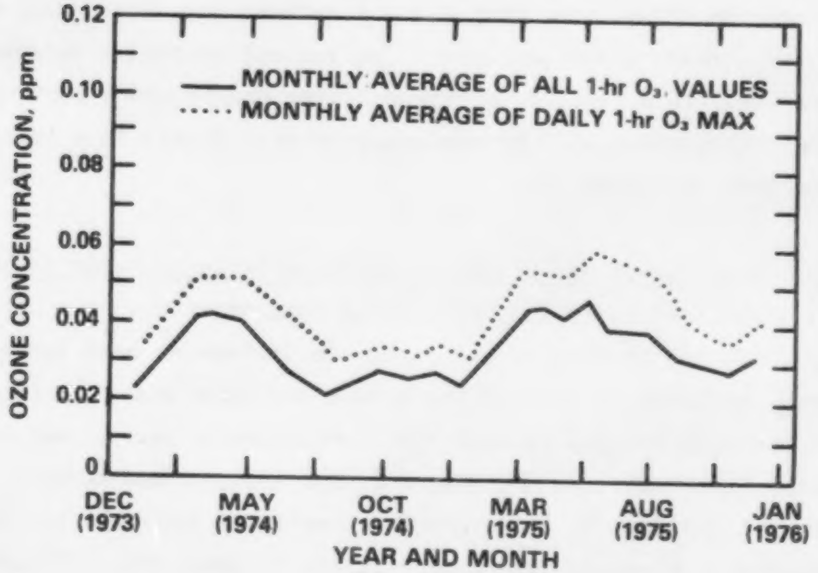


Figure 6-2. Long-term monthly ozone variations at Mauna Loa. Hawaii.

Source: Derived from Singh et al. (1977); cited in U.S. Environmental Protection Agency (1978)

For areas influenced by manmade sources, ozone concentrations tend to follow a long-recognized pattern, with maximum average concentrations occurring mid- to late summer. This pattern is attributable to seasonal meteorological conditions that tend to favor the accumulation of higher concentrations of pollutants and the occurrence of favorable photochemical reaction conditions during the late summer months. Figure 6-3 shows monthly average hourly ozone concentrations for three urban areas, Los Angeles, Denver, and Phoenix, averaged over 1- to 2-year periods prior to 1970. Los Angeles, with a peak concentration in August and a secondary peak in October, and Denver, with a July maximum concentration, both show the typical photochemically related summertime ozone cycle.

An illustration of a nonurban area where the average monthly ozone concentrations seems to follow a typical urban seasonal cycle is shown in Figure 6-4, which depicts 1973-1974 data for Whiteface Mountain in upstate New York. The fact that this region is affected frequently by air masses traveling from the highly urbanized regions located south and southwest of Whiteface Mountain would tend to support strong manmade influences at this site. This cannot be supported specifically for this 1973-1974 time period, however, and some investigators (e.g., Coffey and Stasiuk, 1975a,b) have argued otherwise.

The diurnal concentrations of ozone follow a characteristic pattern in urban source areas. This pattern is one in which the maximum concentrations occur near midday, from the late morning to the early afternoon. Figure 6-5 shows two urban area examples of this diurnal pattern, one from Denver and one from Philadelphia. This sort of pattern is usually explained by the fact that ozone-forming photochemical reactions require several hours to produce a maximum concentration and also that in mid-afternoon atmospheric dilution processes and wind transport usually reach a maximum, thus producing the afternoon decline in concentrations.

At a background site, a midday maximum can also be seen frequently. At such a location the diurnal cycle may result from the photochemical cycle of natural HC and NO_x precursor reactions and/or from the diurnal mixing cycle in which the deeper midday mixing replenishes the ozone concentrations at the surface from the mid-tropospheric layers. This mixing compensates for the ozone scavenged at the earth's surface during the nighttime period of ground-layer stability.

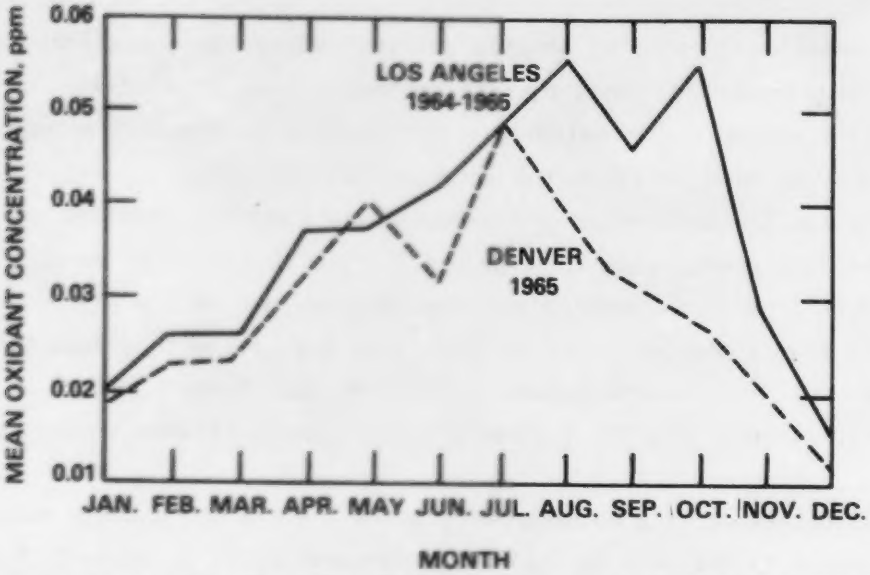


Figure 6-3. Monthly variation of mean hourly oxidant concentrations for Los Angeles and Denver.

Source: U.S. Department of Health, Education, and Welfare (1970), modified

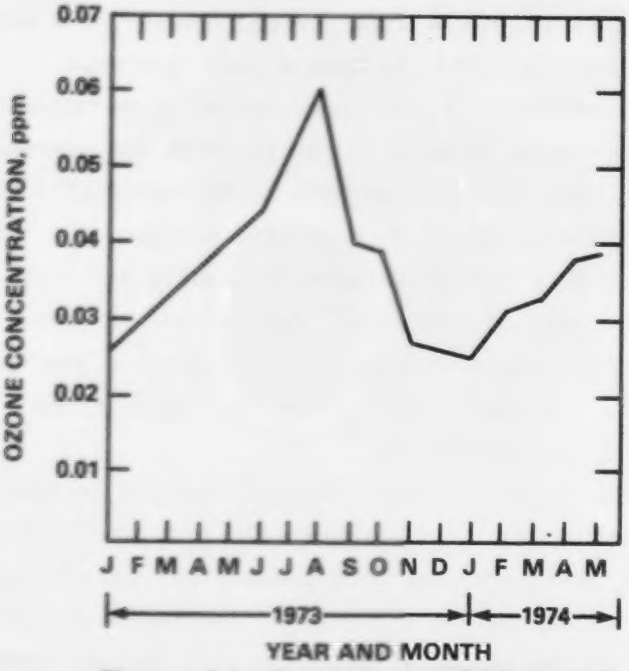


Figure 6-4. Average monthly ozone concentrations recorded at Whiteface Mountain in New York.

Source: Singh et al. (1977); cited in U.S. Environmental Protection Agency (1978)

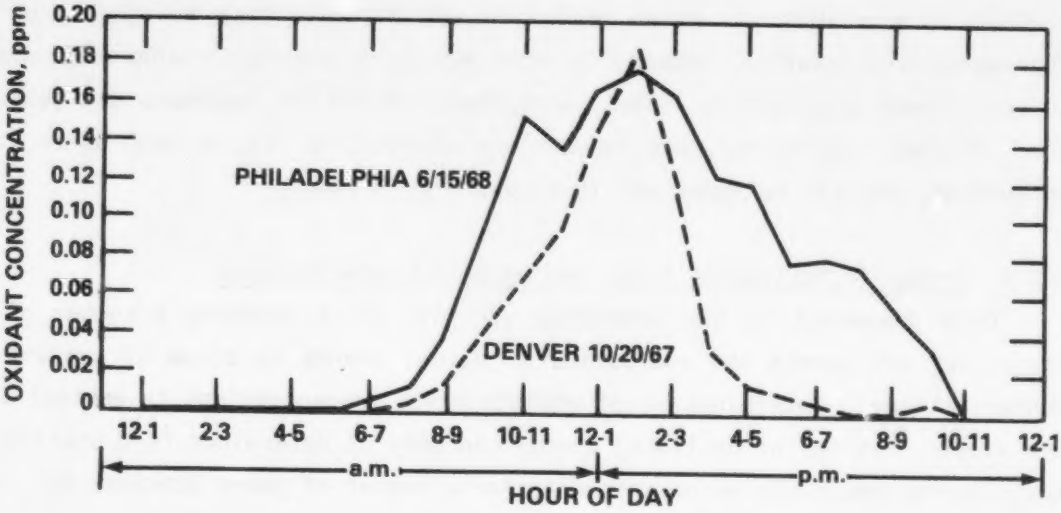


Figure 6-5. Diurnal variation of hourly oxidant concentrations in Philadelphia and Denver.

Source: U.S. Department of Health, Education, and Welfare (1970)

Transport has been mentioned as a factor that influences the urban diurnal cycle. This transport, by horizontal wind movement, serves to reduce the concentration in the source area and to increase subsequently the concentrations in a non-source area at a later time and in a downwind direction. Thus, when the diurnal pattern for a given site shows a peak concentration rather late in the day or at night, it is logical, though not necessarily correct, to attribute this to transport influences.

It also is obvious that the maximum ozone concentrations that are observed at a given site are a complex function of precursor sources and meteorological conditions. Thus, the extrapolation of observational data from one region to another or even within a given region is not a simple task and should be approached with caution, especially when assessing potential ozone exposures to which human populations, crops, ecosystems, and other receptors are subjected. Diurnal, day-to-day, and longer-term seasonal cycles, as well as regional influences, may all be important in exposure assessment.

6.2.4 Trends in Nationwide Ozone and Oxidant Concentrations

Data presented in the preceding section, while covering a number of years, do not permit the evaluation of actual trends in ozone or oxidant concentrations. Determination of whether ozone concentrations in ambient air are static, rising, or declining trends can only be determined from statistical tests using comparable aerometric data for a number of years (chapter 5). The trend in nationwide concentrations of ozone over the period 1975 through 1981 is shown in Figure 6-6 (Hunt and Curran, 1982).

Evaluation of national trends, as well as local or regional trends, in concentrations of ozone in ambient air over the past 5 to 10 years is complicated by several factors: (1) a change in calibration procedure recommended by EPA in 1978 and promulgated in 1979 (see chapter 5); (2) the possible effects on aerometric data of quality assurance procedures instituted by EPA in 1979; (3) the influence of diverse regional meteorological conditions; and (4) changes in precursor emissions.

Figure 6-6 indicates a small decline in the composite average level of the second-highest 1-hour ozone concentration even when the possible effects of the above factors are considered. The 209 sites included in this analysis (Hunt and Curran, 1982) reported at least 50 percent of the possible hourly values in at least 5 of the 7 years from 1975 to 1981.

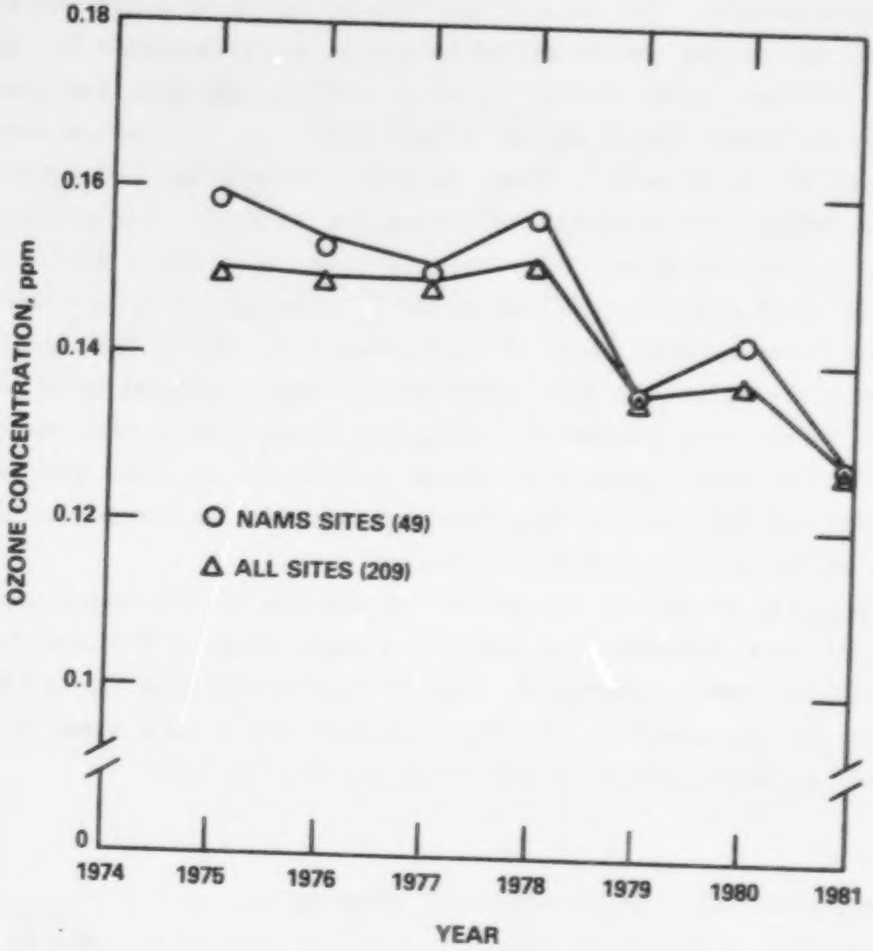


Figure 6-6. National trend in the composite average of the second-highest daily 1-hour ozone concentration, 1975 through 1981.

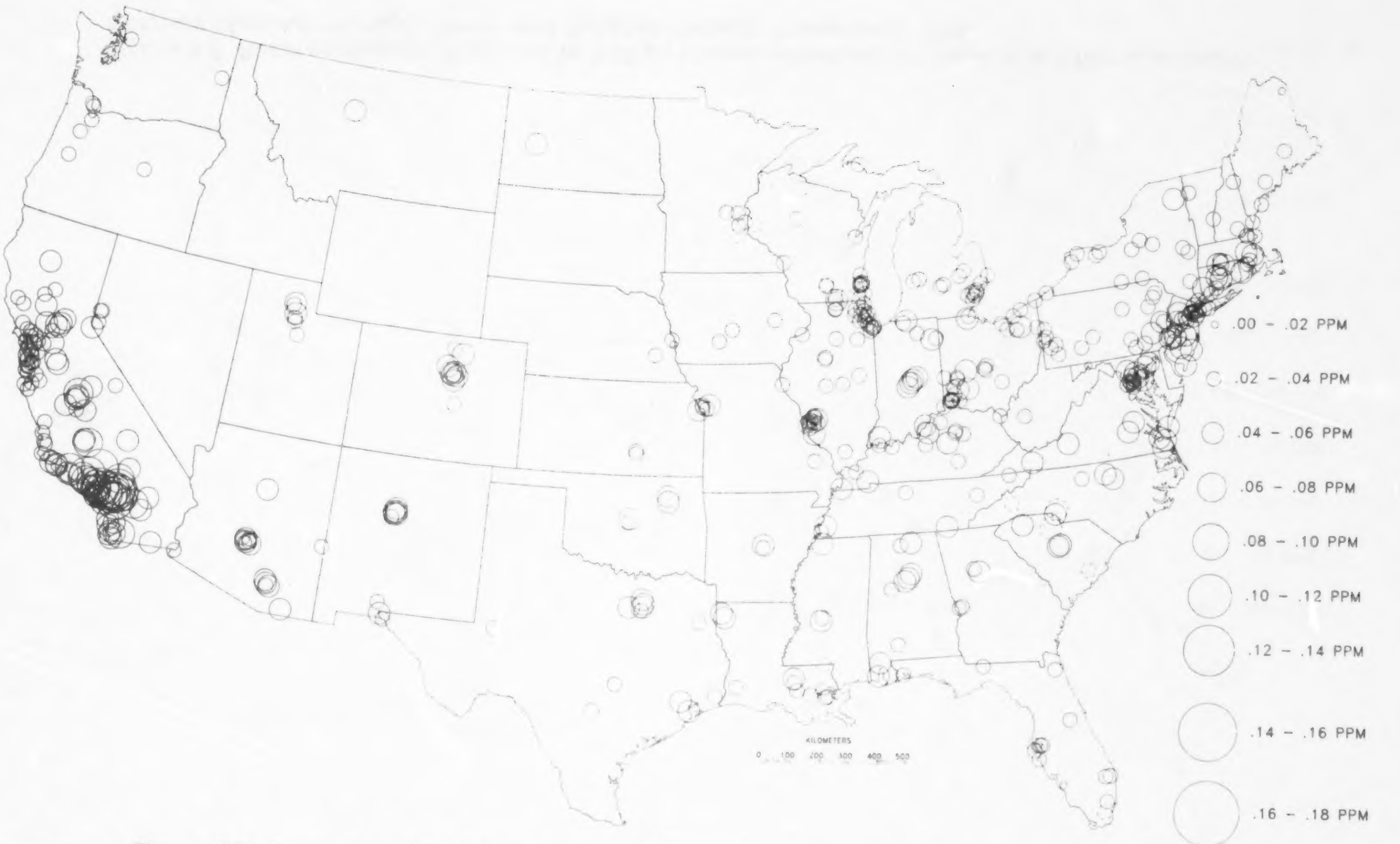
Source: Hunt and Curran (1982)

Assessment of how much of the observed decline in ozone concentrations from 1975 through 1981 should be attributed to the 1979 promulgation of the ultraviolet (UV) calibration method as the Federal Reference Method is not a simple matter of applying a correction factor to existing aggregated aerometric data. The monitoring practices at each of the 209 sites would have to be examined in detail. Not all monitoring sites switched to the use of the UV method simultaneously. The state of California, for example (in EPA Region IX), had already been using the UV method before it was promulgated in February 1979. In addition, other states, in other regions, may have used the boric acid-potassium iodide (BAKI) method before, after, or both before and after promulgation of the UV method, since the BAKI procedure was allowed by EPA as an interim method for 18 months following the 1979 UV promulgation (see chapter 5). Likewise, other states used gas-phase titration prior to 1979 but either BAKI or UV procedures following the UV promulgation. The relationship among these three methods, even if monitoring practices at individual sites were known, is complex and would preclude the simple application of a single correction factor (see chapter 5). Hunt and Curran (1982) have noted that Region IX is the only region that showed improvement in ozone air quality between 1980 and 1981 but not long-term improvement. California, whicn dominates Region IX, changed calibration in 1975.

The majority of ambient air monitoring stations in the nation are operated by state and local agencies, but there is a small group of National Air Monitoring Stations (NAMS) (chapter 5) that is responsible directly to EPA. The trend line for the subset of 49 NAMS ozone stations is also shown in Figure 6-6 and tracks fairly closely the line for all 209 stations.

6.3 OVERVIEW OF OZONE CONCENTRATIONS IN URBAN AREAS

An overview of nationwide urban ozone concentrations for 1981 is provided in Figures 6-7 and 6-8, which depict graphically average daylight concentrations. Figure 6-7 shows data for spring and summer months, the months which comprise the smog season in most if not all areas of the nation, and Figure 6-8 shows daylight concentrations during the fall and winter months. The daylight period of 6:00 a.m. to 8:00 p.m. includes the hours of greatest human activity outdoors; the hours when exposure of vegetation and ecosystems would be expected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.10 - .12 PPM
.12 - .14 PPM
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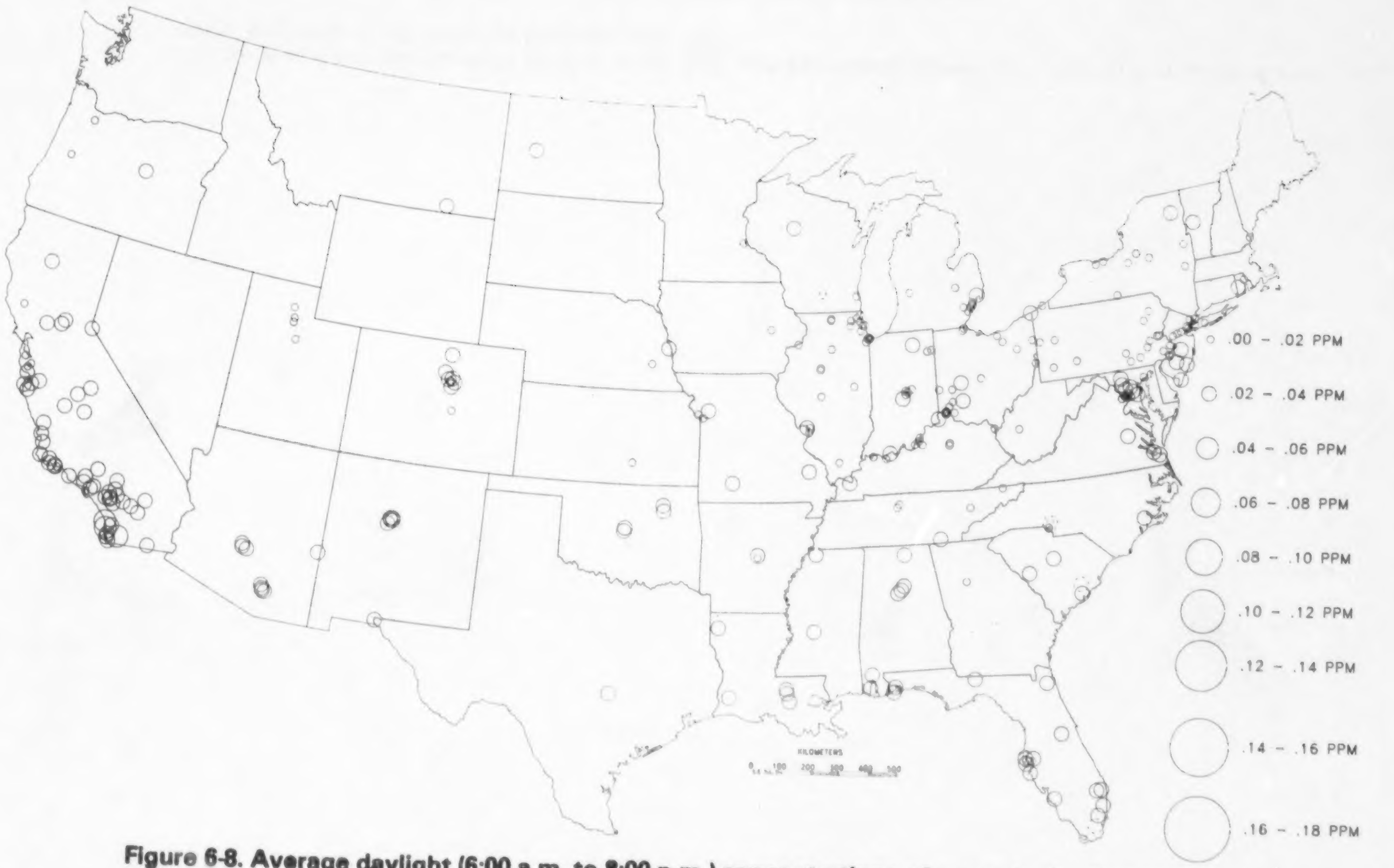
.16 - .18 PPM
KILOMETERS
0 100 200 300 400 500
01 Apr 1983

Figure 6-7. Average daylight (6:00 a.m. to 8:00 p.m.) concentrations of ozone in the second and third quarters (April through September), 1981.

Source: G. Duggan, OAQPS, U.S. Environmental Protection Agency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.16 - .18 PPM
KILOMETERS
0 100 200 300 400 500
01 Apr 1983

Figure 6-8. Average daylight (6:00 a.m. to 8:00 p.m.) concentrations of ozone in the first and fourth quarters (January through March and October through December), 1981.

Source: G. Duggan, OAQPS, U.S. Environmental Protection Agency to have the greatest consequences (stomata are open in daylight and photosynthesis is taking place; see chapter 7); and the hours of greatest local formation of ozone and other oxidants via photochemistry in the atmosphere (see chapter 4). The average concentrations during the spring and summer months (second and third quarters of the year) are clustered mainly in the 0.04 to 0.06 ppm range. Averages for the winter and fall months (first and fourth quarters) are clustered mainly in the 0.02 to 0.04 ppm range, which is within the range of natural background concentrations.

The stations used in Figures 6-7 and 6-8 reported at least 75 percent of the possible 1-hour values per quarter. Some stations, however, monitor ozone only during the months when the potential for photochemical ozone formation is significant in those localities. Also, certain areas of the United States are not monitored routinely for ozone because of the lack of emission sources or transport events and thus the low potential for significant ozone or oxidant concentrations. The Great Basin and the Great Plains, for example, are such areas.

Figure 6-9 shows the collective nationwide frequency distribution of the second highest 1-hour O_3 concentration for 1979, 1980, and 1981. Only data collected by the Federal Reference Method (chemiluminescence) or the equivalent UV method (see chapter 5) have been used in this analysis. A "valid site" is one reporting at least 75 percent of the 8760 possible 1-hour values in a year. There were 282 such sites in 1979, 266 in 1980, and 358 in 1981 (U.S. Environmental Protection Agency, 1980, 1981, 1982). As shown by Figure 6-9, 50 percent of the second-highest 1-hour values in this 3-year period were 0.12 ppm or less and 10 percent were equal to or greater than 0.20 ppm. While the third-highest values are also of interest, the highest and second-highest 1-hour values are of greater consequence in relation to the existing ozone standard and, thus, in relation to their health and welfare implications. The second-highest value determines whether an area is in compliance with the present ozone standard.

Table 6-6 lists the second-highest 1-hour O_3 values reported for 1979 through 1982 for the 80 most populous Standard Metropolitan Statistical Areas (SMSAs), grouped by population. Collectively these SMSAs account for 54 percent of the 1980 United States population of 226.5 million. The significant observation to be drawn from this table of second-highest values is that the lowest median concentration in 1981, 0.12 ppm for SMSAs having populations of

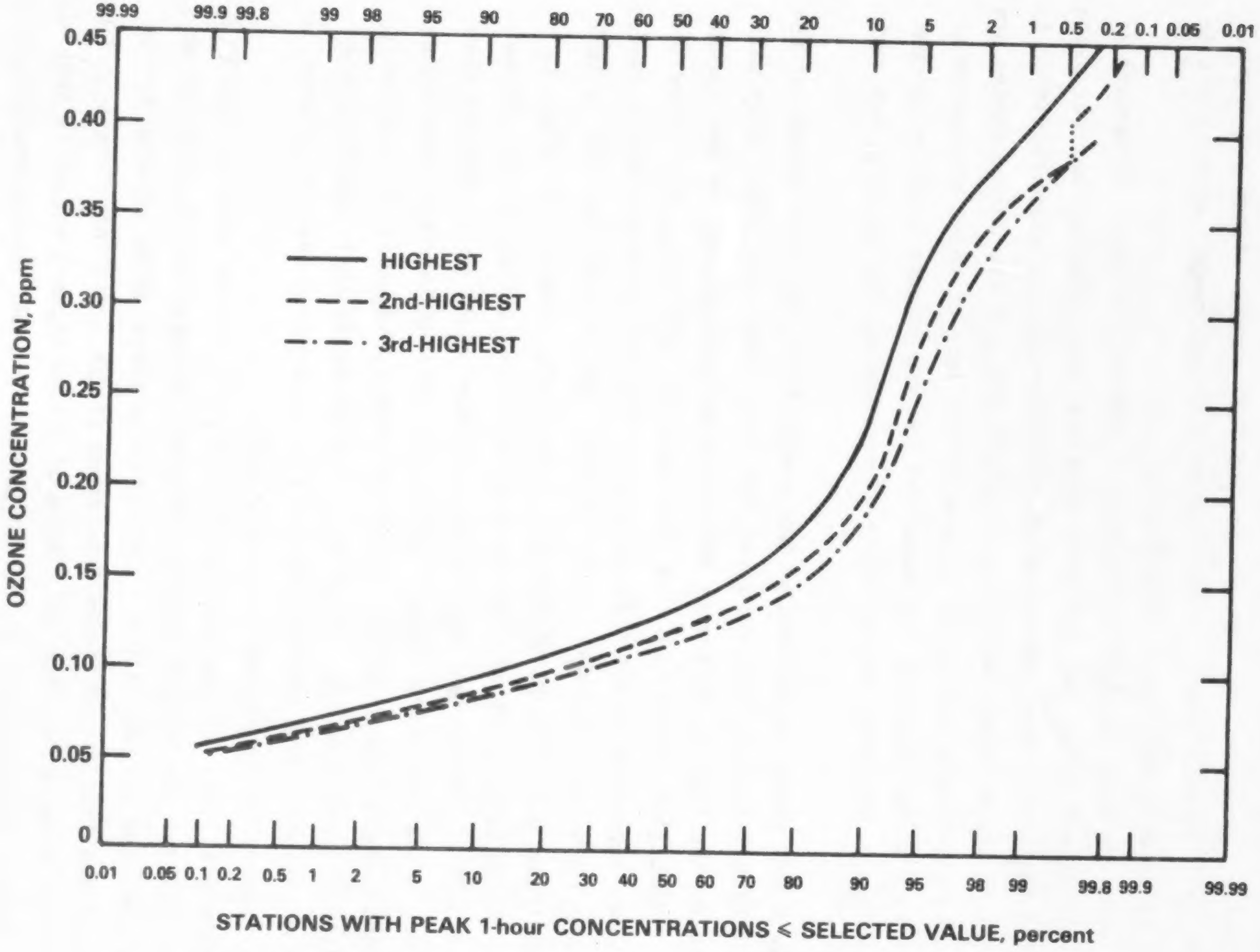


Figure 6-9. Collective distributions of the three highest 1-hour ozone concentrations for 3 years (1979, 1980, and 1981) at valid sites (906 station-years).

Source: U.S. Environmental Protection Agency, SAROAD data files for 1979, 1980, 1981

TABLE 6-6. SECOND-HIGHEST 1-hour OZONE CONCENTRATIONS REPORTED FOR 80 STANDARD METROPOLITAN STATISTICAL AREAS HAVING POPULATIONS $\geq$0.5 MILLION

Standard Metropolitan Statistical Area	Ozone concentration, ppm			
	1979	1980	1981	1982
Population $\geq$2 million				
New York, NY - NJ	0.19	0.18	0.18	0.17
Los Angeles - Long Beach, CA	0.44	0.44	0.35	0.32
Chicago, IL	0.22[a]	0.34	0.14	0.12
Philadelphia, PA - NJ	0.18[a]	0.24[a]	0.17	0.18
Detroit, MI	0.12[a]	0.15	0.15	0.16
San Francisco - Oakland, CA	0.14	0.18	0.14	0.14
Washington, DC - MD - VA	0.18[a]	0.19	0.15	0.15
Dallas - Fort Worth, TX	0.17	0.18	0.15	0.17
Houston, TX	0.24	0.30	0.23	0.21
Boston, MA	0.22[a]	0.15	0.13	0.16[a]
Nassau - Suffolk, NY	0.18	0.17	0.14	0.13
St. Louis, MO - IL	0.16[a]	0.18	0.15	0.15
Pittsburgh, PA	0.17[a]	0.17[a]	0.16	0.14
Baltimore, MD	0.14[a]	0.18[a]	0.17	0.14
Minneapolis - St. Paul, MN - WI	0.10[a]	0.13	0.10	0.10
Atlanta, GA	0.16	0.15	0.14	0.14
Summary statistics:				
Minimum 1-hour value	0.10	0.13	0.10	0.10
Median 1-hour value	0.175	0.18	0.15	0.15
Maximum 1-hour value	0.44	0.44	0.35	0.32
Population 1 to < 2 million				
Newark, NJ	0.15	0.15	0.14	0.17
Anaheim - Santa Ana - Garden Grove, CA	0.35	0.29	0.31	0.18
Cleveland, OH	0.14[a]	0.12	0.12	0.12
San Diego, CA	0.36	0.22	0.24	0.21
Miami, FL	0.05[a]	0.15	0.14	0.14
Denver - Boulder, CO	0.16	0.13	0.13	0.14
Seattle - Everett, WA	0.13	0.09	0.12	0.09
Tampa - St. Petersburg, FL	0.11	0.13	0.11	0.11
Riverside - San Bernardino - Ontario, CA	0.42	0.38	0.34	0.32
Phoenix, AZ	0.12[a]	0.15	0.16	0.12
Cincinnati, OH - KY - IN	0.13	0.16	0.13	0.13
Milwaukee, WI	0.17	0.14	0.17	0.13
Kansas City, MO - KS	0.12[a]	0.16	0.12	0.10
San Jose, CA	0.17	0.19	0.14	0.14
Buffalo, NY	0.11[a]	0.14	0.12	0.11
Portland, OR - WA	0.11	0.10	0.15	0.12
New Orleans, LA	0.12	0.12	0.11	0.17
Indianapolis, IN	0.12	0.14	0.13	0.12
Columbus, OH	0.10	0.12	0.11	0.13

TABLE 6-6. SECOND-HIGHEST 1-hour OZONE CONCENTRATIONS REPORTED FOR 80 STANDARD METROPOLITAN STATISTICAL AREAS HAVING POPULATIONS $\geq$0.5 MILLION (continued)

Standard Metropolitan Statistical Area	Ozone concentration, ppm			
	1979	1980	1981	1982
San Juan, PR	ND[b]	ND[b]	0.07	0.02
San Antonio, TX	0.11	0.12	0.12	0.14
Fort Lauderdale - Hollywood, FL	0.10[a]	0.12	0.11	0.09
Sacramento, CA	0.16[a]	0.17	0.17	0.16
Summary statistics:				
Minimum 1-hour value	0.05	0.09	0.07	0.02
Median 1-hour value	0.125	0.14	0.13	0.13
Maximum 1-hour value	0.42	0.38	0.34	0.32
Population 0.5 to < 1 million				
Rochester, NY	0.12	0.12	0.12	0.11
Salt Lake City - Ogden, UT	0.15	0.17	0.15	0.14
Providence - Harwick - Pawtucket, RI - MA	0.17	0.21	0.15	0.15
Memphis, TN - AR - MS	0.11[a]	0.13	0.12	0.12
Louisville, KY - IN	0.16[a]	0.19	0.14	0.17
Nashville - Davidson, TN	0.09[a]	0.13	0.13	0.11
Birmingham, AL	ND[b]	0.16	0.16	0.15
Oklahoma City, OK	0.11[a]	0.12	0.11	0.11
Dayton, OH	0.14[a]	0.13	0.12	0.16
Greensboro - Winston-Salem - High Point, NC	0.10[a]	0.12	0.11	0.11
Norfolk - Virginia Beach - Portsmouth, VA - NC	0.10	0.12	0.11	0.10
Albany - Schenectady - Troy, NY	0.13	0.13	0.13	0.12
Toledo, OH - MI	0.15	0.14	0.13	0.12
Honolulu, HI	0.04[a]	0.04	0.04	0.04
Jacksonville, FL	0.13	0.12	0.10	0.11
Hartford, CT	0.20	0.24	0.15	0.16
Orlando, FL	0.10[a]	0.09	0.10	0.09
Tulsa, OK	0.13	0.15	0.15	0.13
Akron, OH	0.15	0.11	0.24	0.14
Gary - Hammond - East Chicago, IN	0.13[a]	0.15	0.14	0.13
Syracuse, NY	0.13[a]	0.11	0.11	0.12
Northeast Pennsylvania	0.11	0.15	0.10	0.16
Charlotte - Gastonia, NC	0.12[a]	0.14	0.12	0.12
Allentown - Bethlehem - Easton, PA - NJ	0.17[a]	0.15	0.12	0.14
Richmond, VA	0.13[a]	0.13	0.12	0.12
Grand Rapids, MI	0.11	0.11	0.11	0.11
New Brunswick - Perth Amboy - Sayreville, NJ	0.10[a]	0.19	0.13	0.16
West Palm Beach - Boca Raton, FL	0.08[a]	0.09	0.09	0.09
Omaha, NE - IA	0.10[a]	0.14	0.08	0.09
Greenville - Spartanburg, SC	0.11[a]	0.11	0.11	0.11
Jersey City, NJ	0.15[a]	0.16	0.14	0.14
Austin, TX	0.12[a]	0.13	0.12	0.11

TABLE 6-6. SECOND-HIGHEST 1-hour OZONE CONCENTRATIONS REPORTED FOR 80 STANDARD METROPOLITAN STATISTICAL AREAS HAVING POPULATIONS ≥0.5 MILLION (continued)

Standard Metropolitan Statistical Area	Ozone concentration, ppm 1979	1980	1981	1982
Youngstown - Warren, OH	0.13	0.12	0.13	0.11
Tucson, AZ	0.10	0.10	0.12	0.12
Raleigh - Durham, NC	0.10[a]	0.13	0.12	0.09
Springfield - Chicopee - Holyoke, MA - CT	0.16[a]	0.15	0.16	0.15
Oxnard - Simi Valley - Ventura, CA	0.19	0.18	0.20	0.22
Wilmington, DE - NJ - MD	0.16[a]	0.17[a]	0.12[a]	0.16
Flint, MI	0.11	0.11	0.11	0.11
Fresno, CA	0.18	0.19[a]	0.17	0.16
Long Branch - Asbury Park, NJ	0.14[a]	0.16[a]	ND[b]	ND[b]
Summary statistics:				
Minimum 1-hour value	0.04	0.04	0.04	0.04
Median 1-hour value	0.13	0.13	0.12	0.12
Maximum 1-hour value	0.20	0.24	0.27	0.22

[a] Fewer than 90 days of data.

[b] ND = no data.

Source: U.S. Environmental Protection Agency, SAROAD data files for 1979-1982

0.5 to 1 million, equals the current national ambient air quality standard for ozone. The suggestion of an increase with increasing population is largely the disproportionate influence of southern California SMSAs having populations greater than 1 million.

6.4 OVERVIEW OF OZONE CONCENTRATIONS IN NONURBAN AREAS

As mentioned in the preceding section, very few ozone monitoring stations are located in nonurban areas. Consequently, the aerometric data base for nonurban areas is not comparable to that for urban areas. The nonurban data presented in this section were obtained from two special-purpose monitoring networks that were designed to provide ozone concentrations at sites specifically selected to represent a variety of pristine or rural nonurban environments. These sites do not all represent areas totally unaffected by manmade ozone or its precursors, as shown by the fact that some data records contain a significant number of high values that are best explained as resulting from the transport of ozone or its precursors from upwind urban areas. The data given here are intended to show an overview of nonurban concentrations in areas with relatively infrequent urban influences. Additional data on specific rural areas are presented in sections 6.5.1 and 6.5.2.

6.4.1 National Air Pollution Background Network (NAPBN)

The NAPBN consists of eight stations located in eight National Forests (NF) across the country (Figure 6-10). The first three stations began operation in 1976 (Green Mountain NF, Vermont; Kisatchie NF, Louisiana; and Custer NF, Montana); the second three in 1978 (Chequamegon NF, Wisconsin; Mark Twain NF, Missouri; and Croatan NF, North Carolina); and the last two in 1979 (Apache NF, Arizona; and Ochaco NF, Oregon). Yearly summaries of ozone concentrations through 1980 are shown in Table 6-7 for the three sites established first (Evans et al., 1983). The principal points of interest in these summary statistics are the range of ozone concentrations and the arithmetic mean of the values measured at these National Forest sites. The arithmetic mean concentrations for the three sites ranged from 0.027 ± 0.015 ppm at the Kisatchie NF site in 1979 to 0.040 ± 0.011 ppm at the Custer NF site in 1979. The arithmetic mean across all years and all three sites is 0.033 ppm. Fluctuations in the observed concentrations from year-to-year and site-to-site are demonstrated by

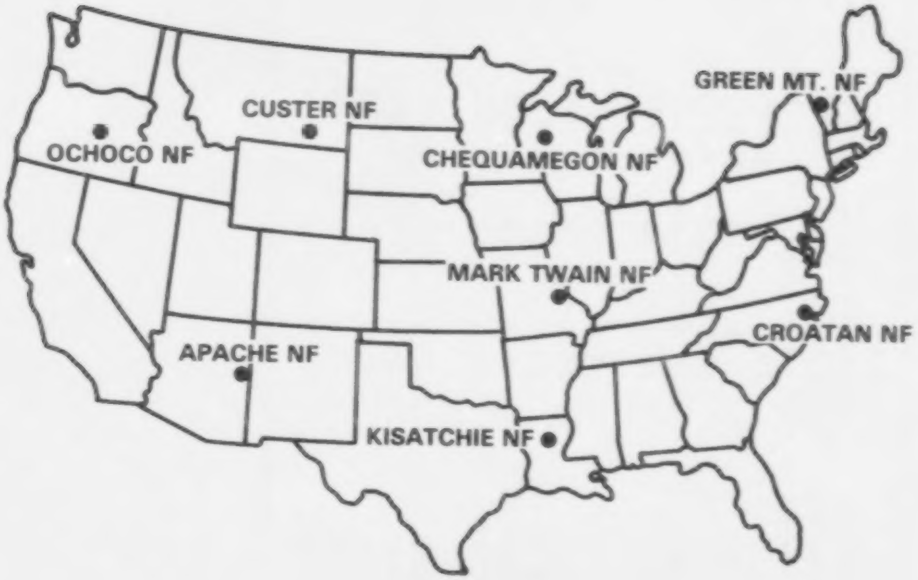

GREEN MT. NF
CUSTER NF
OCHOCO NF
CHEQUAMEGON NF
MARK TWAIN NF
CROATAN NF
APACHE NF
KISATCHIE NF

Figure 6-10. Locations of the eight national forest (NF) stations comprising the National Air Pollution Background Network (NAPBN).

Source: Evans et al. (1983)

TABLE 6-7. ANNUAL OZONE SUMMARY STATISTICS FOR THREE NAPBN SITES

Site	Year	No. 1-hour measurements	% of possible 1-hr meas.	Conc., ppm		Conc., ppm		Conc., ppm	
				Min.	Max.	Arith. Mean	Arith. std. dev.	Geom. mean	Geom. std. dev.
Kisatchie NF, LA	1976	3448	39.4	LD[a]	0.125	0.032	0.021	0.024	2.19
	1977	6793	77.5	LD	0.135	0.033	0.023	0.025	2.25
	1978	5636	64.3	LD	0.125	0.034	0.021	0.027	2.14
	1979	6993	79.8	LD	0.100	0.027	0.015	0.023	1.92
	1980	4438	50.7	LD	0.105	0.028	0.016	0.023	1.94
Custer NF, MT	1976	275	3.1	0.020	0.060	0.039	0.008	0.038	1.22
	1977	7603	86.8	LD	0.080	0.040	0.011	0.039	1.37
	1978	7674	87.6	LD	0.075	0.030	0.017	0.023	2.14
	1979	8488	96.9	LD	0.070	0.032	0.012	0.029	1.59
	1980	7754	88.5	LD	0.070	0.037	0.012	0.035	1.41
Green Mt. NF, VT	1976	1058	12.1	LD	0.060	0.029	0.011	0.026	1.76
	1977	6483	74.0	LD	0.145	0.038	0.021	0.031	2.00
	1978	3671	41.9	LD	0.105	0.029	0.018	0.024	2.01
	1979	6423	73.3	LD	0.105	0.032	0.017	0.027	1.86
	1980	8574	97.9	LD	0.115	0.032	0.017	0.027	1.90

[a] LD = less than detectable.

Source: Evans et al. (1983)

the range of concentrations measured and by the size of the standard deviations as well. The lowest concentrations seen were below the limits of detection of the chemiluminescence monitor employed, but the highest concentrations observed at the Kisatchie NF and Green Mt. NF sites were both above the present ozone standard of 0.12 ppm.

These summary statistics show somewhat higher mean concentrations, lower maximum concentrations, and lower standard deviations in data obtained at the Custer NF site than at the other two, which may indicate that meteorological conditions are less variable at that site or that the site is much less affected, if not altogether unaffected, by manmade ozone or its precursors. Previous data shown in Table 6-5 for Wolf Point, Montana, are generally consistent with the Custer NF data.

During a 6-day period in 1979, the NAPBN site in the Mark Twain NF, Missouri, showed ozone concentrations well in excess of typical values. A 1-hour value of 0.125 ppm, the maximum observed at any NAPBN site in 1979, was measured at that site on July 21, 1979. Evans et al. (1983) have calculated the trajectories of air masses reaching the site during the 6-day period of July 18 through July 23, 1979. They ascribed the unusually high values, including the peak value on the 21st, to pollutants picked up as the trajectory passed over urban areas in the Ohio River Valley and the Great Lakes region. Table 6-8 shows the peak 1-hour value for each of the 6 days. Figure 6-11 shows the trajectories for the air parcels reaching the Mark Twain NF site at midnight (0000), 8 a.m. (0800), noon (1200), and 6 p.m. (1800) on July 21, 1979. On July 23, clouds and rain spread over the region and the air-flow trajectories shifted to the east and south, reducing both the quantities of transported precursors and the potential for photochemical ozone generation.

6.4.2 Sulfate Regional Experiment Sites (SURE)

As part of a comprehensive air monitoring project sponsored by the Electric Power Research Institute (Martinez and Singh, 1979) ozone data were collected by the chemiluminescence method in the last 6 months of 1977 at the nine "nonurban" SURE sites in the eastern United States shown in Figure 6-12. On the basis of diurnal NO_x patterns that indicated the influence of traffic emissions, five of the sites were classed as "suburban"; the other four were classed as "rural." The ozone data from these nine stations are summarized in Table 6-9. Martinez and Singh (1979) noted that the four rural stations

TABLE 6-8. CONCENTRATIONS OF OZONE DURING 6-day PERIOD OF HIGH VALUES AT NAPBN SITE IN MARK TWAIN NATIONAL FOREST, MISSOURI, 1979

Date	1-hr maximum O_3 concentration, ppm
July 18	0.080
July 19	0.100
July 20	0.115
July 21	0.120
July 22	0.125
July 23	0.050

Source: Evans et al. (1983)

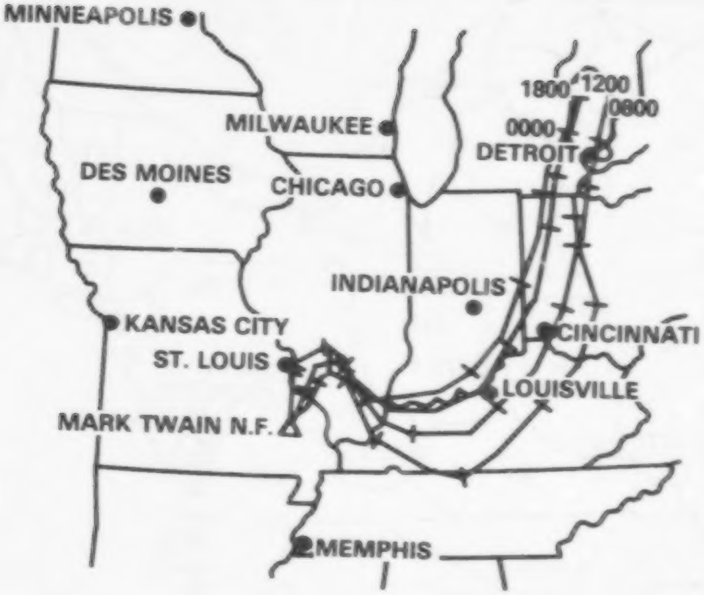
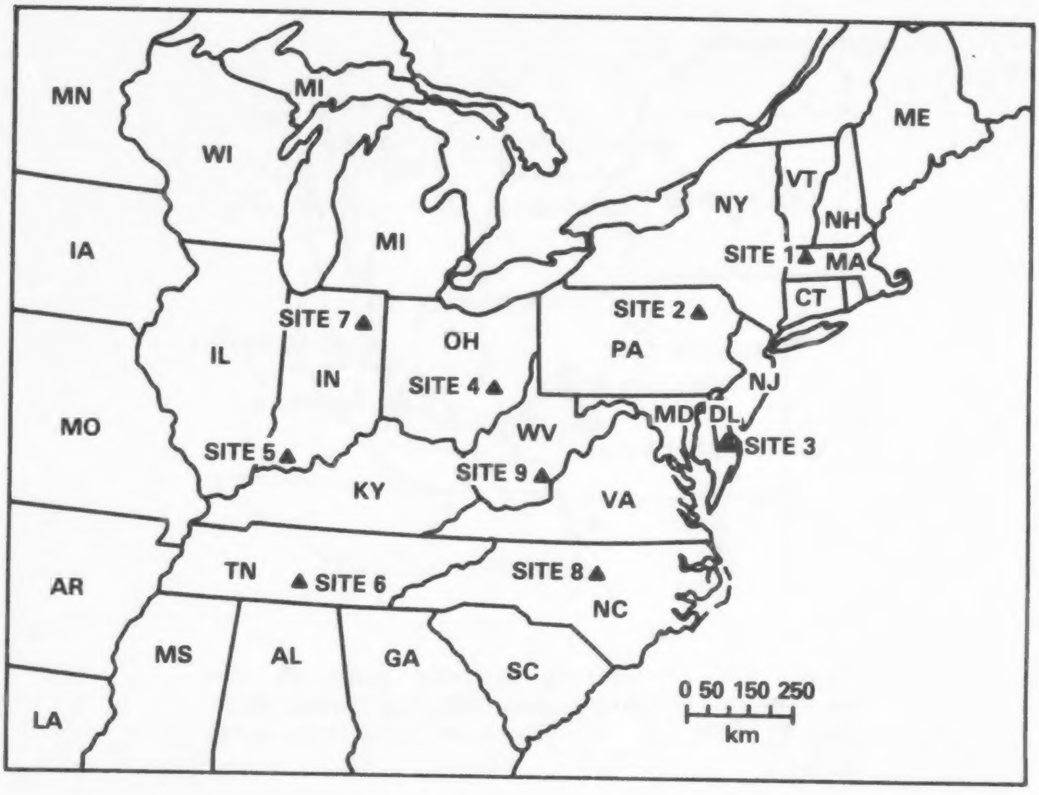

MINNEAPOLIS
1800
1200
0600
0000
MILWAUKEE
DETROIT
DES MOINES
CHICAGO
INDIANAPOLIS
KANSAS CITY
CINCINNATI
ST. LOUIS
LOUISVILLE
MARK TWAIN N.F.
MEMPHIS

Figure 6-11. Trajectory analysis plots at the NAPNB site at Mark Twain National Forest, MO, July 21, 1979 (distance between bars represents 12 hr).


MN
WI
MI
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MO
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SITE 7
SITE 4
SITE 5
KY
WV
SITE 9
VA
PA
SITE 2
NY
SITE 1
VT
NH
MA
CT
ME
NJ
MD
DL
SITE 3
AR
TN
SITE 6
SITE 8
NC
MS
AL
GA
SC
LA
0 50 150 250
km

Figure 6-12. Location of SURE Monitoring Stations.

Source: Martinez and Singh (1979)

TABLE 6-9. SUMMARY OF OZONE CONCENTRATIONS MEASURED AT SULFATE REGIONAL EXPERIMENT (SURE) NONURBAN STATIONS, AUGUST THROUGH DECEMBER 1977

	Total no. of measurements	Number of measurements with concentrations:			Mean concn,. ppm	Mean of daily 1-hour maxima, ppm	1-hour maximum, ppm
		>0.08 ppm	>0.10 ppm	>0.12 ppm			
Rural sites							
#1 Montague, MA	3419	60	33	21	0.021	0.044	0.153
#4 Duncan Falls, OH	3441	52	2	0	0.029	0.049	0.107
#6 Giles Co., TN	3632	63	5	0	0.026	0.052	0.117
#9 Lewisburg, WV	3459	23	3	0	0.035	0.054	0.106
Suburban sites							
#2 Scranton, PA	3410	0	0	0	0.023	0.035	0.077
#3 Indian River, DE	3017	29	0	0	0.030	0.049	0.099
#5 Rockport, IN	3462	29	0	0	0.025	0.046	0.099
#7 Ft. Wayne, IN	3438	0	0	0	0.020	0.039	0.080
#8 Research Triangle Park, NC	3495	80	10	0	0.025	0.050	0.118

Source: Martinez and Singh (1979)

occasionally recorded high values comparable with urban areas, but that the incidence was low. They concluded that infrequent transport of ozone or its precursors, or both, rather than local ozone generation, was the most probable cause of these high values.

6.5 VARIATIONS IN OZONE CONCENTRATIONS: DATA FROM SELECTED URBAN AND NONURBAN SITES

Variations of ozone concentrations by season and by time of day, as discussed qualitatively in section 6.2, have been long known and are well documented. First studied in smog chambers, diurnal patterns have since been corroborated by field investigations, and exceptions to such general patterns have been examined and documented. Likewise, field investigations have substantiated general seasonal patterns and exceptions to them, and have also established a number of spatial variations in concentration, such as those that occur with latitude or with altitude. While it is difficult to discuss temporal and spatial variations separately, this section is subdivided along those lines for convenience.

6.5.1 Temporal Variations in Ozone Concentrations

In section 6.2, diurnal and seasonal data for ozone concentrations were presented as reported in the 1978 criteria document for ozone and other photochemical oxidants. More recent data showing such temporal variations in ozone concentrations will be reported here to provide a more detailed discussion.

6.5.1.1 Diurnal Variations in Ozone Concentrations. By definition, diurnal variations are those that occur during a 24-hour period. Diurnal patterns of ozone may be expected to vary with location, depending on the balance among the factors affecting ozone formation, transport, and destruction. Figure 6-13 shows the diurnal pattern of ozone concentrations on July 13, 1979, in Philadelphia, Pennsylvania. On this day a peak 1-hour average concentration of 0.20 ppm, the highest for the month, was reached at 2:00 p.m., presumably as the result of local photochemical processes. The severe depression of concentrations to below detection limits (less than 10 ppb) between 3:00 and 6:00 a.m. is usually explained as resulting from the scavenging of ozone by local nitric oxide emissions. In this regard, this station is typical of most urban locations.

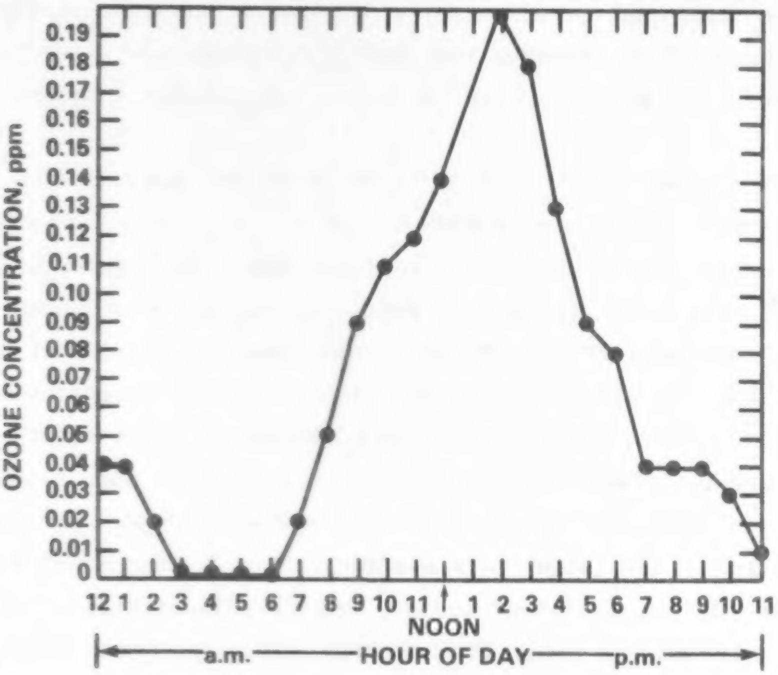

Figure 6-13. Diurnal pattern of 1-hour ozone concentrations on July 13, 1979, Philadelphia, PA.

Source: U.S. Environmental Protection Agency, SAROAD data file for 1979

Diurnal profiles of ozone concentrations can vary from day to day at a specific site because of changes in the various factors that influence concentrations. Such day-to-day variations are clearly demonstrated in Figure 6-14, which shows diurnal variations in ozone concentrations on 2 consecutive days at the same monitoring site in Detroit, Michigan. Differences in timing and magnitude occur that are especially noticeable between midnight and about 7:00 a.m. Transport is probably involved in these nighttime variations. The afternoon peaks, the actual maxima for the 2 days, differ in magnitude but not in timing.

Composite diurnal data, that is, concentrations for each hour of the day averaged over multiple days or months, often differ markedly from the diurnal cycle shown by concentrations for a specific day. In Figures 6-15 through 6-18, diurnal data for 2 consecutive days are compared with composite diurnal data (1-month averages of hour-by-hour measurements) at each of two urban (Washington, D.C., and St. Louis County, Missouri) and two agriculture-oriented sites (Alton, Illinois, and N. Little Rock, Arkansas). Several obvious points of interest present themselves in these graphs: (1) at some sites at least, peaks can occur at virtually any hour of the day or night but these may not show up strongly in the longer-term average data; (2) some sites may experience multiple peaks during a 24-hour period; and (3) disparities, some of them large, can exist between peaks (the diurnal data) and the 1-month mean (the composite diurnal data) of hourly ozone concentrations. These are only examples of the differences that can occur between daily and monthly mean concentration patterns. Since these patterns differ from site to site, no conclusions about comparative levels at a given site or between urban and rural sites can be drawn from these figures, especially since the rural and suburban data in these examples come from months generally considered to be outside the photochemical smog season.

The effects of averaging are readily apparent when diurnal ozone concentrations are compared with "composite diurnal" ozone concentrations. Figures 6-19 and 6-20, based on 3-month averages, demonstrate rather graphically, when compared with Figures 6-15 through 6-18 (daily values and 1-month averages) the effects of lengthening the period of time over which values are averaged. The figures show composite diurnal patterns calculated on the basis of 3 months. While seasonal differences are seen, and will be discussed later, the comparison of 3-month and 1-month composite diurnal concentrations

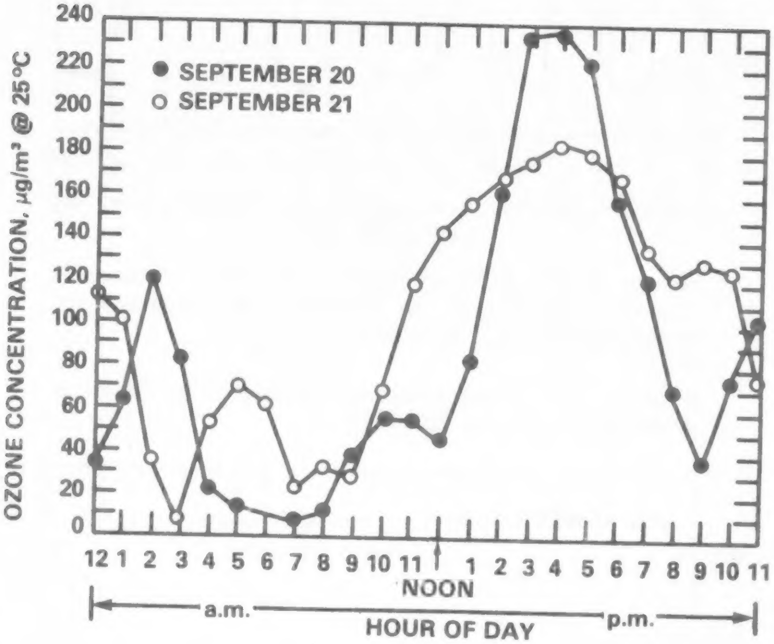

Figure 6-14. Diurnal patterns of ozone concentrations, September 20 and 21, 1980, Detroit, MI. (1960 μg/m³ = 1 ppm)

Source: U.S. Environmental Protection Agency, SAROAD data file for 1980

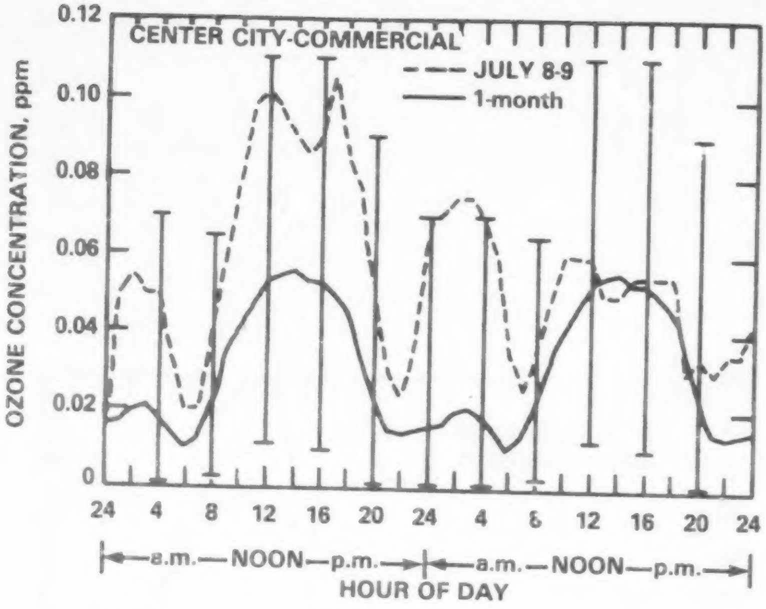

Figure 6-15. Diurnal and 1-month composite diurnal variations in ozone concentrations, Washington, DC, July 1981.

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

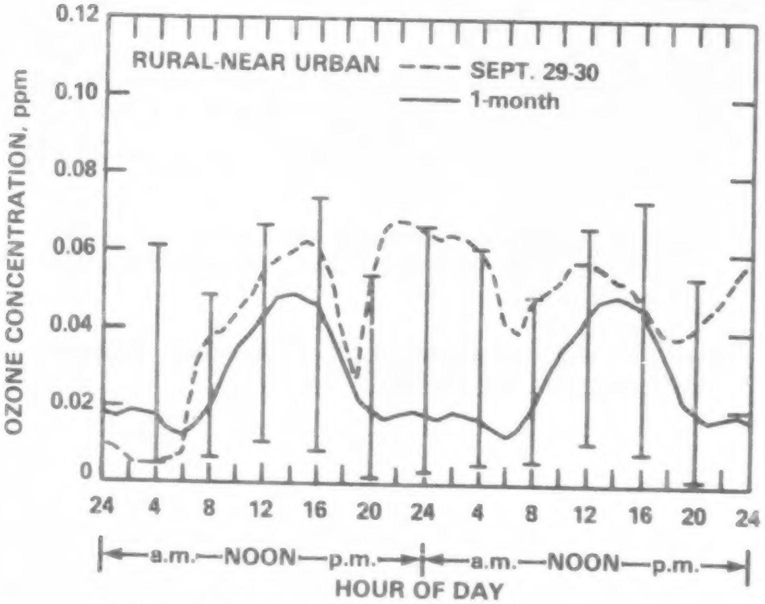

Figure 6-16. Diurnal and 1-month composite diurnal variations in ozone concentrations, St. Louis County, MO, September 1981.

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

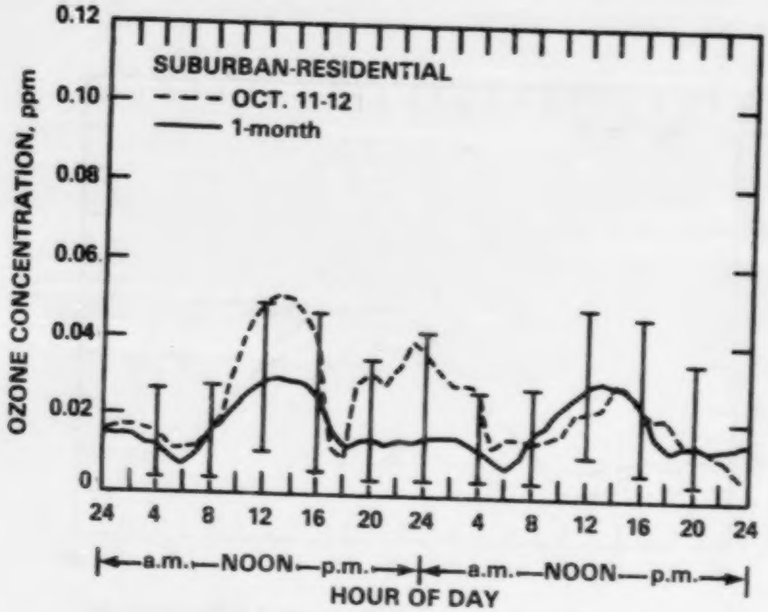

Figure 6-17. Diurnal and 1-month composite diurnal variations in ozone concentrations, Alton, IL, October 1981 (fourth quarter).

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

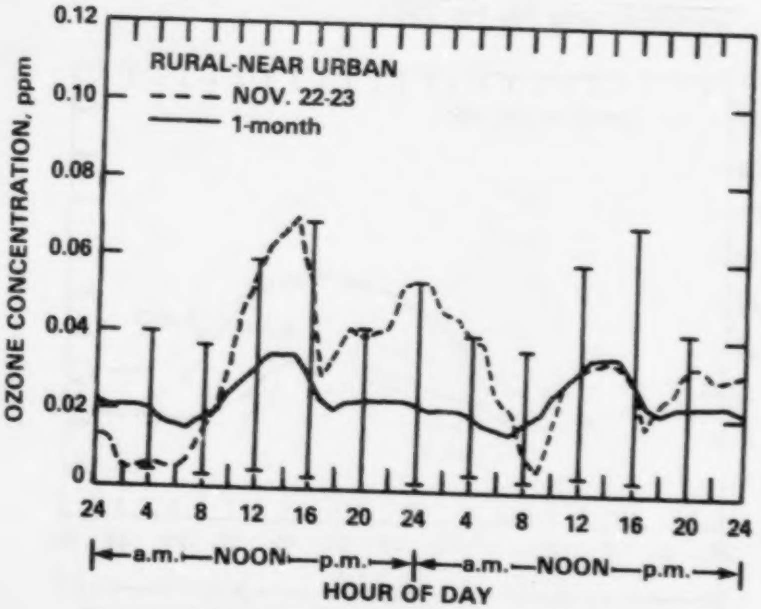

Figure 6-18. Diurnal and 1-month composite diurnal variations in ozone concentrations, N. Little Rock, AR, November 1981 (fourth quarter).

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

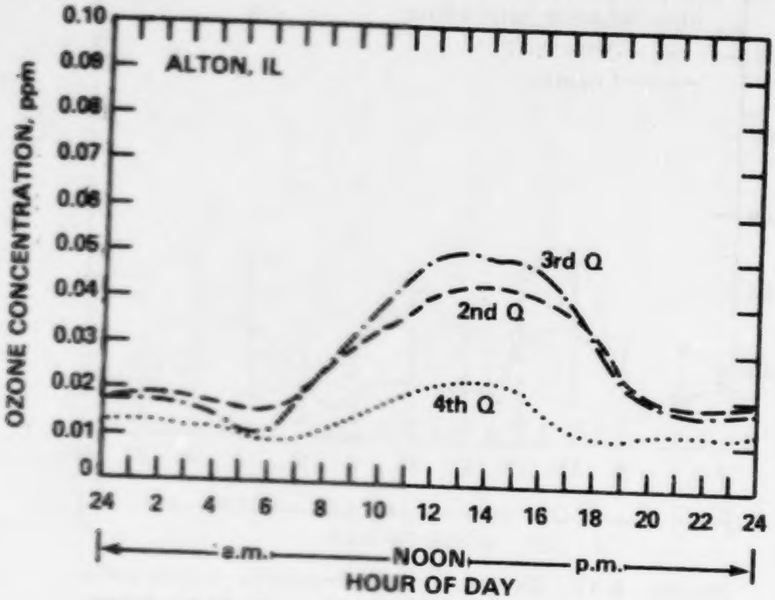

Figure 6-19. Composite diurnal patterns by quarter of ozone concentrations at a rural agricultural site, Alton, IL, 1981.

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

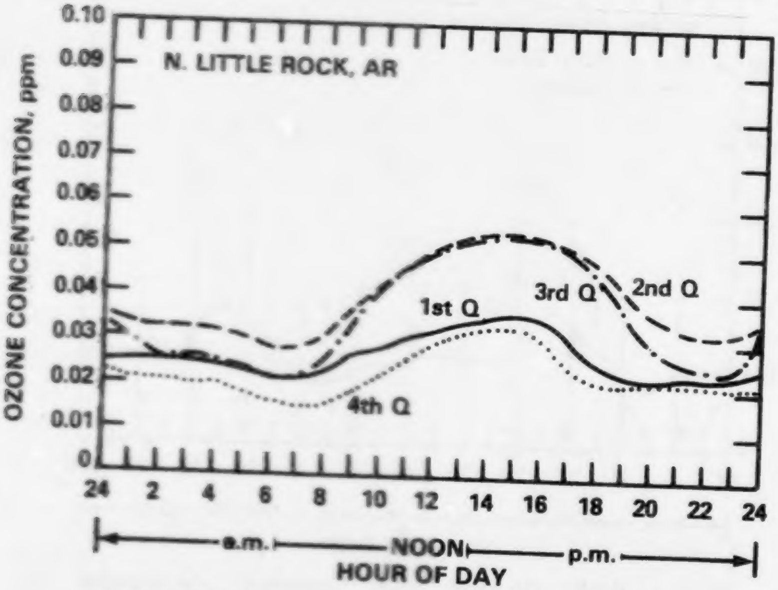

Figure 6-20. Composite diurnal patterns by quarter of ozone concentrations at a rural agricultural site, N. Little Rock, AR, 1981.

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

at the same sites readily demonstrates the smoothing out of peak concentrations as the averaging period is lengthened. Thus, a fourth pertinent point of interest, related to the third point, emerges from the data presented above: that is, increasing the averaging time obscures the magnitude and time of occurrence of peak ozone concentrations. This is an obvious and familiar result in the statistical treatment of sampling data, but one that is highly pertinent to the protection of human health and welfare from the effects of ozone.

Quantitative analyses of the relationships among 1-hour peak concentrations or second-highest 1-hour peak concentrations and daylight, diurnal, monthly, seasonal, and yearly average ozone concentrations lie outside the scope of this document. The relationships of peak and mean concentrations assume more or less significance, depending upon whether the health and welfare effects of exposure to ozone are solely concentration-dependent, heavily concentration-dependent, or both concentration- and time-dependent. Nevertheless, if acute exposures are the chief cause of adverse health and welfare effects, careful attention will have to be paid to the relationship of 1-hour versus other averaging times.

Regarding other points of interest seen in these several figures, the significance of the occurrence of peak concentrations outside of daylight hours is lessened by the fact that most people spend the nighttime hours indoors and the fact that the stomata of green plants are apparently closed at night. (Gradients between indoor and outdoor concentrations of ozone, relative to human exposures, are briefly discussed in section 6.5.2. The relationship of stomatal function to the effects observed with ozone exposure of green plants is discussed in chapter 7.)

No attempt is made in this section to document the respective contributions of local formation of ozone versus transport of ozone; however, the occurrence of multiple peak ozone concentrations within a 24-hour period is usually construed as indicating the presence of ozone transported to the site from elsewhere (as discussed in chapter 4). An illustration of the diurnal variations that are seen when transport occurs is shown by Figure 6-21, where dual peaks occur on each of three successive days at a site of the Sulfate Regional Experiment (SURE) network.

An example is shown in Figure 6-21 of the occurrence of dual peaks of high ozone concentrations on each of 3 consecutive days of high concentrations.

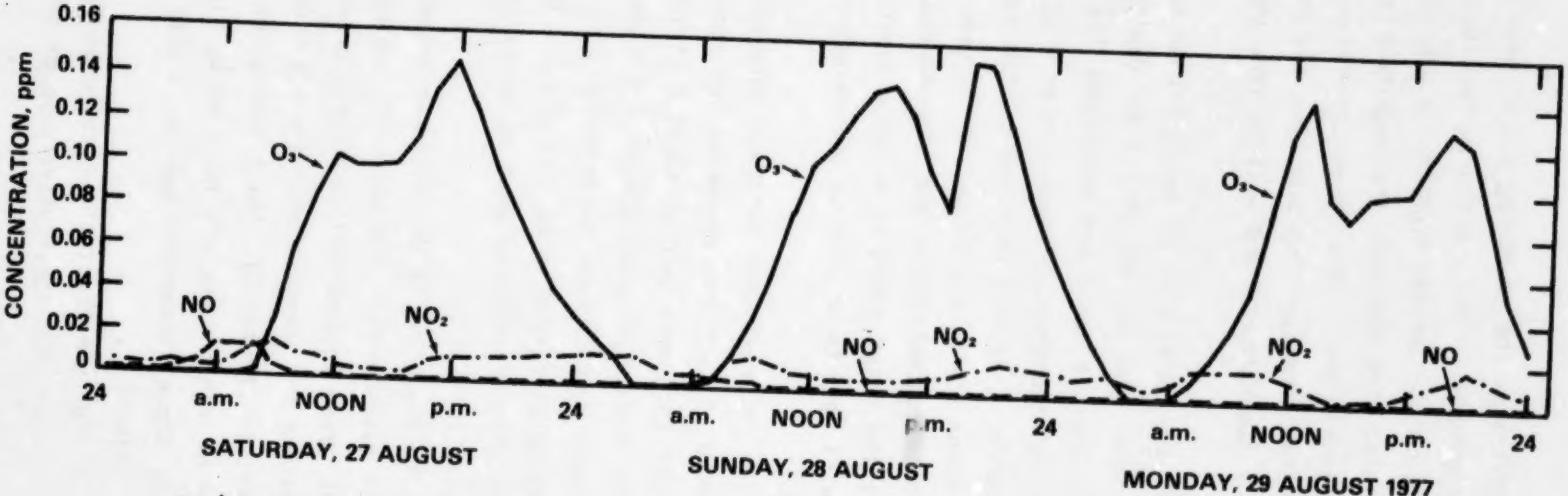

Figure 6-21. Three-day sequence of hourly ozone concentrations at Montague, MA, SURE station showing locally generated midday peaks and transported late peaks.

Source: Singh and Martinez (1979)

One of the more important questions regarding the effects of ozone on both people and plants is the possible significance of high concentrations lasting 1 hour or longer on each of 2 or more consecutive days.

In human controlled exposures, attenuation of response to ozone has been observed at about 0.20 to 0.50 ppm in exercising subjects upon repeated, consecutive-day exposures (see chapter 11). That attenuation is lost after exposures to those levels cease (see chapter 11 for the time course of loss of attenuation). This finding raises the important question of what patterns of repeated ambient air exposures might be experienced by communities in high-ozone areas, as well as in other parts of the country.

Data records for 6:00 a.m.-to-8:00 p.m. ozone concentrations in the second and third quarters of the year, 1979 through 1981, have been examined for Pasadena and Pomona, California; Dallas, Texas; and Washington, D.C. These cities were chosen because adequate aerometric data records were available, because they represent areas known to experience high ozone concentrations (California), and because they represent different geographic regions of the country (west, southwest, east). Similar data could be compiled for any city for which sufficient aerometric data exist. The choice of the daylight period and of the second and third quarters is consistent with known diurnal (see Figure 6-22) and seasonal patterns (Figures 6-19 and 6-20) of ozone concentrations and with patterns of typical human and crop or ecosystems exposures. One can count from the data records the number of exposures to ozone that occur for respective durations (2, 3, 4, etc., consecutive days) at concentrations equal to or greater than specified concentration ranges. A cumulative tally of such consecutive-day exposures results in the kind of data shown in Table 6-10. Plotting of the cumulative number of exposures of respective durations (in days) for respective concentration cutoffs produces the log-probability graphs shown in Figures 6-23 through 6-26.

For this discussion, an _n_-day period at or above the concentration cutoffs is simply called an "exposure" and an _n_-day period below the respective cutoffs is called a "respite."

The intuitive expectation is that for successively higher daily concentration limits, the number of "exposures" in a given time at a given place will become smaller and the length of the intervening "respites" will increase. Table 6-10 shows that this expectation is supported by data from a number of locations across the country. This table shows that the total number of days

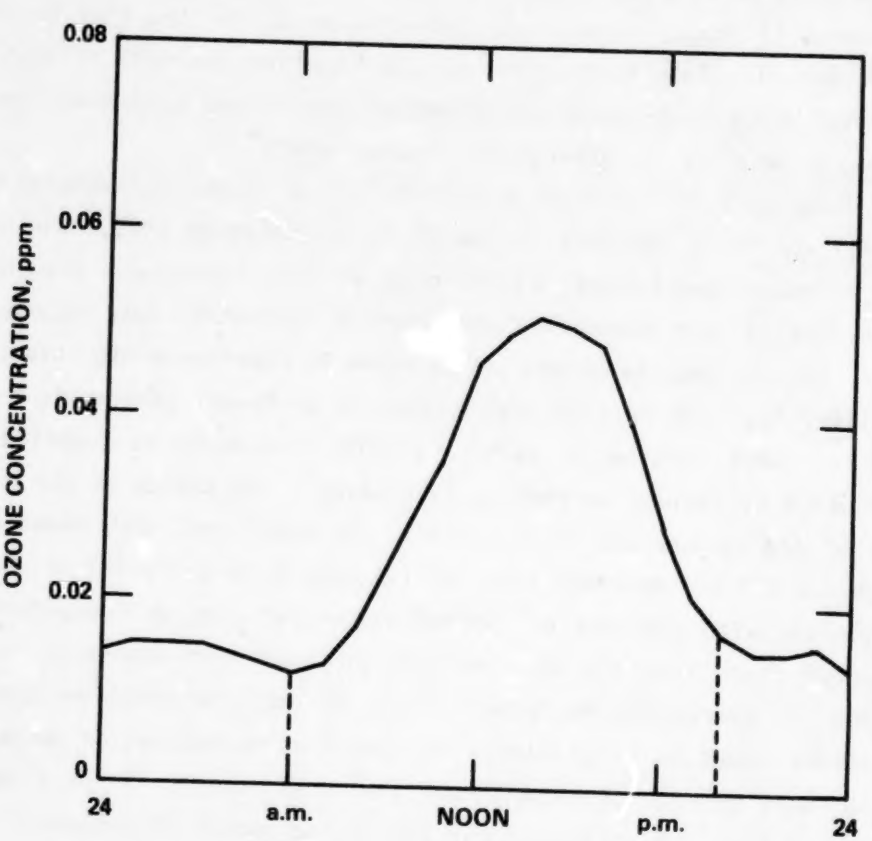

Figure 6-22. Composite diurnal ozone pattern at an Argonne, IL, agricultural site, August 6 through September 30, 1980.

Source: Kress and Miller (1983)

TABLE 6-10. TOTAL DAYS WHEN MAXIMUM DAILY OZONE CONCENTRATION EXCEEDED OR WAS LESS THAN SPECIFIED CONCENTRATIONS APRIL THROUGH SEPTEMBER, 1979 THROUGH 1981, AT PASADENA AND POMONA, CALIFORNIA, AND AT WASHINGTON, D.C., AND DALLAS, TEXAS

Location	Concentration (ppm)					
	<0.06	≥ 0.06	<0.12	≥ 0.12	<0.18	≥ 0.18
Pasadena, CA	44	488	160	372	303	229
Pomona, CA	70	472	207	335	373	169
Washington, DC	296	146	437	5	442	0
Dallas, TX	124	327	412	39	449	2

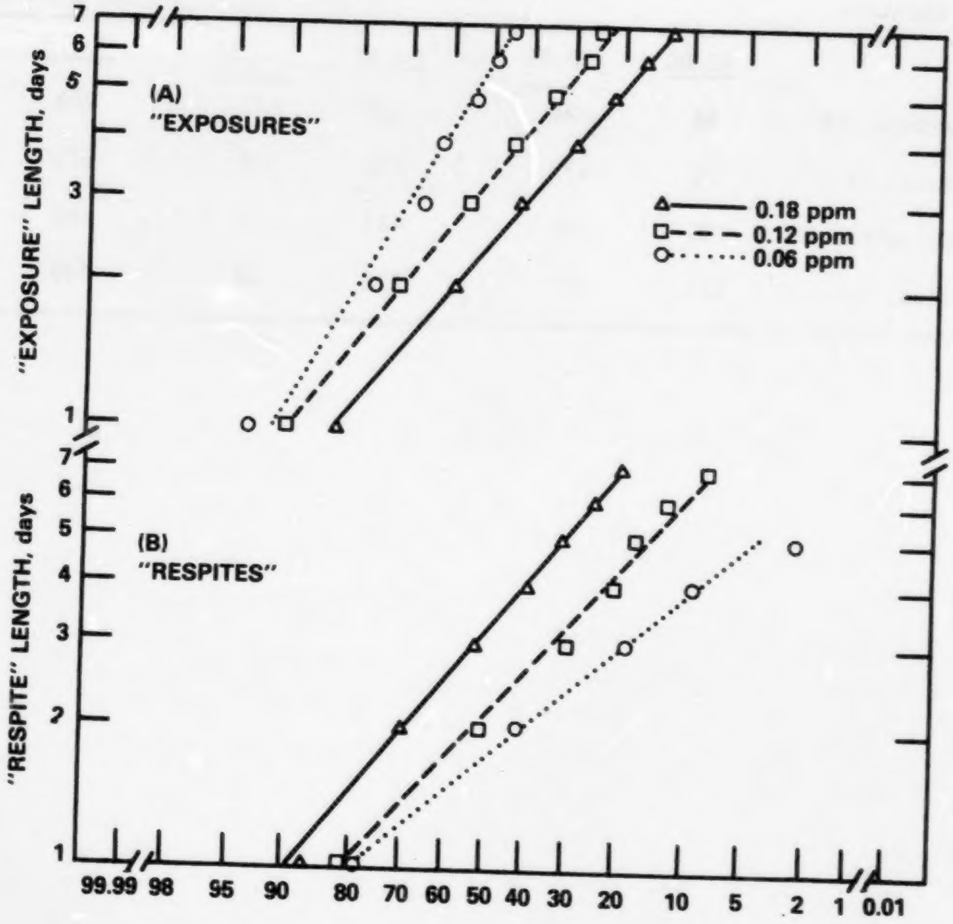

Figure 6-23. Probability that "exposures" and "respites" for specified concentration cutoffs will persist for indicated or longer period at Pasadena, CA, based on aerometric data for April through September, 1979 through 1981.

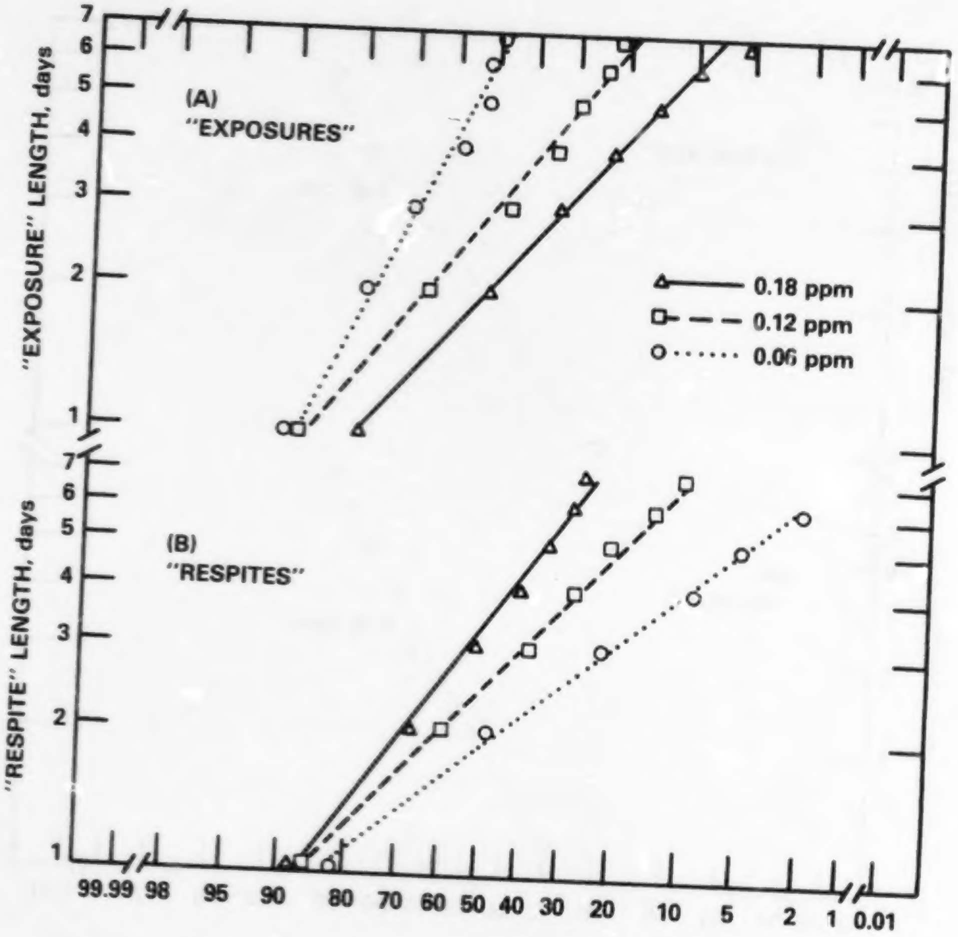

Figure 6-24. Probability that "exposures" and "respites" for specified concentration cutoffs will persist for indicated or longer period at Pomona, CA, based on aerometric data for April through September, 1979 through 1981.

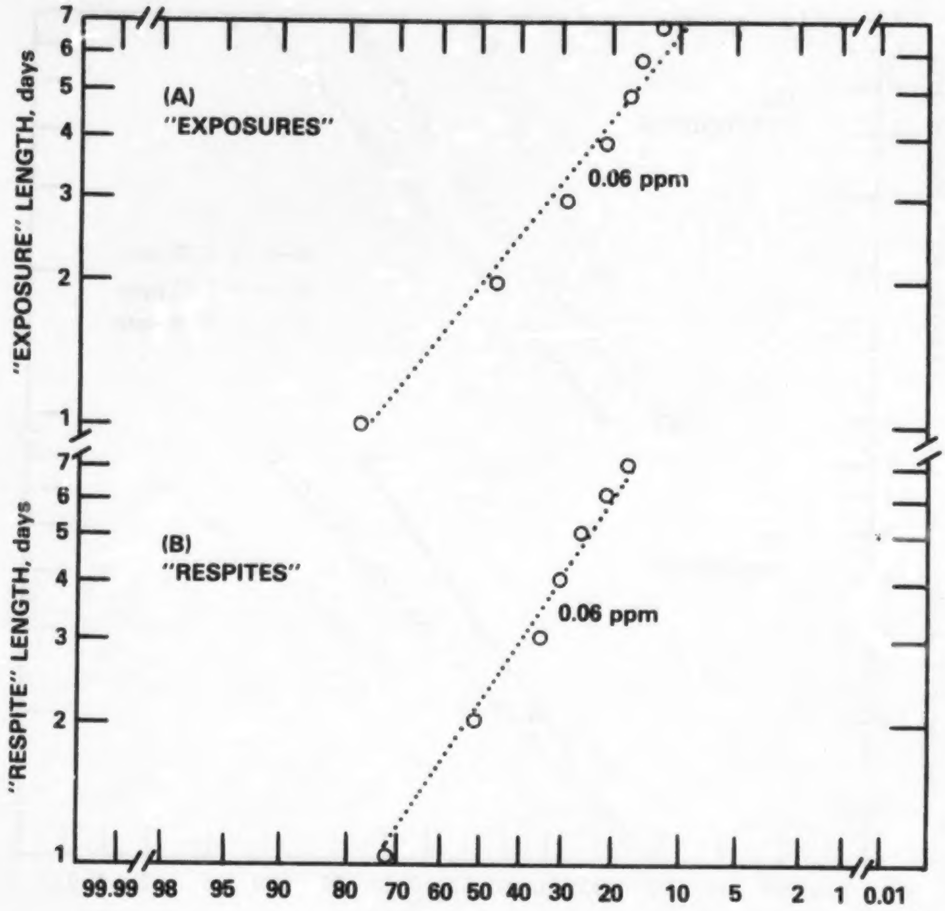

Figure 6-25. Probability that "exposures" and "respites" for specified concentration cutoffs will persist for indicated or longer period at Washington, DC, based on aerometric data for April through September, 1979 through 1981.

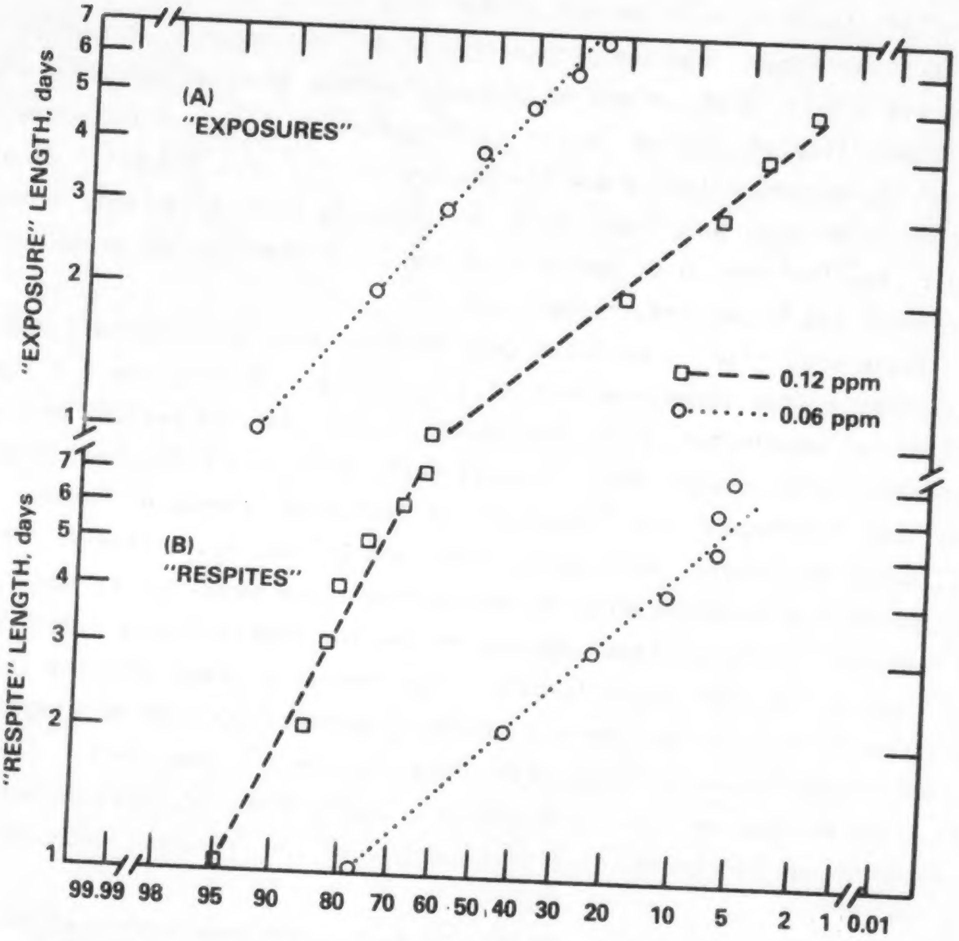

Figure 6-26. Probability that "exposures" and "respites" for specified concentration cutoffs will persist for indicated or longer period at Dallas, TX, based on aerometric data for April through September, 1979 through 1981.

associated with "exposures" decreases as the limiting concentration increases, and vice versa for "respite" days. Figure 6-23 shows that for Pasadena the lengths in days of "exposures" and "respites" have log-probability distributions. For example, this distribution of Pasadena "exposures" and "respites" shows that there is a 70 percent probability that a 0.06 ppm "exposure" will be 3 days or longer; and the probability of an "exposure" of 3 days or longer is 55 percent for 0.12 ppm and 42 percent for 0.18 ppm. As would be expected, the probability of a given length of "respite" at Pasadena increases with increasing concentration; and while the probability of a "respite" at a concentration lower than 0.06 and 3 days or longer is only 18 percent, a 3-day or longer "respite" from 0.12 ppm or 0.18 ppm concentrations has probabilities of 34 percent and 52 percent, respectively.

Table 6-10 also shows total days of occurrence ("exposures") and relief ("respites") from concentrations of 0.06, 0.12, and 0.18 ppm for Pomona, California; Washington, D.C.; and Dallas, Texas, for the period April through September, 1979 through 1981. Figures 6-24, 6-25, and 6-26 show the probabilities that "exposures" and "respites" of indicated lengths or numbers of days will occur for Pomona, Washington, D.C., and Dallas, respectively. The results for Pomona are not especially different from those shown for Pasadena, as might be expected for sites close together in the Los Angeles basin. Both Washington, D.C. and Dallas show significantly fewer "exposure" days than the California stations at each of the three limiting concentrations; and Washington, D.C. actually experienced no "exposures" equal to the 0.18 ppm limit. The probability plots for Washington, D.C., and Dallas (Figures 6-25 and 6-26) do not show results for the higher concentration limits because of the few occurrences in these categories.

These tabulations and probability plots have been presented to show the probable distribution of concentrations by number of consecutive days for these specific sites. These are descriptive, based on 3 years of data at these specific sites. These tabulations and figures cannot be used to predict the probable concentration that might accompany a given "exposure" or "respite" duration.

6.5.1.2 Seasonal Variations in Ozone Concentrations. In addition to the diurnal cycles and between-day variations discussed in the preceding section, seasonal variations in ozone concentrations occur (for the reasons discussed in chapter 4) and usually assume characteristic patterns.

In order to compile an assessment of potential ozone damage to the six leading commercial crops in the United States (corn, soybeans, hay, wheat, cotton, and tobacco), Lefohn (1982) surveyed 304 ozone monitoring stations and identified 24 that (1) were located in counties producing significant quantities of one or more of these six crops in 1978; (2) reported at least 50 percent of possible hourly data in 1978; (3) reported an hourly maximum of at least 0.1 ppm O_3; and (4) ranked high in cumulative ozone exposure for the period April to October, 1978. Six of these sites represented counties high in soybean, wheat, or hay production. Quarterly composite diurnal patterns for 6 of these sites with reasonably complete ($\geq$75 percent) 1981 data are shown in Figure 6-27 (U.S. Environmental Protection Agency, SAROAD file). The average levels are apparently comparable with the long-term averages at the NAPBN sites previously discussed (section 6.4.1). In addition, the diurnal patterns for these sites clearly show the clustering of the afternoon levels into two seasons, the low "winter" levels in the first and fourth quarters and the higher "summer" levels in the second and third quarters of the year.

Although averaging causes details to be obscured, the average diurnal patterns in Figure 6-27 show that the time of occurrence of peaks differs among sites. Among the sites shown in Figure 6-27, ozone concentrations appear to peak at 2:00 to 2:30 p.m. in Little Rock in the higher-concentration second and third quarters. At Bakersfield in the second and third quarters, there is evidence, even in these smoothed-out curves, of two peaks, the first at about 1:00 p.m. and the second at 5:00 to 6:00 p.m. At the Clark County, Ohio, site, the peak concentrations in the second and third quarters center around about 5:00 p.m., but they do not return to "baseline" until after midnight. These patterns appear to indicate transport into the areas. It is also possible that single peaks that are shifted to mid- to late afternoon are the product of transport. Depending upon proximity to urban centers and wind speed and direction, rural areas usually experience their peak concentrations later than those of urban areas, often but not always, within daylight hours.

Composite diurnal variations in ozone concentrations at a rural site in Argonne, Illinois, over a 7-week period of the third quarter of 1980 were shown in Figure 6-22. The actual day-to-day variations in ozone concentration over the entire third quarter of 1980 at that site are shown for comparison in Figure 6-28. As part of the National Crop Loss Assessment Network, the site

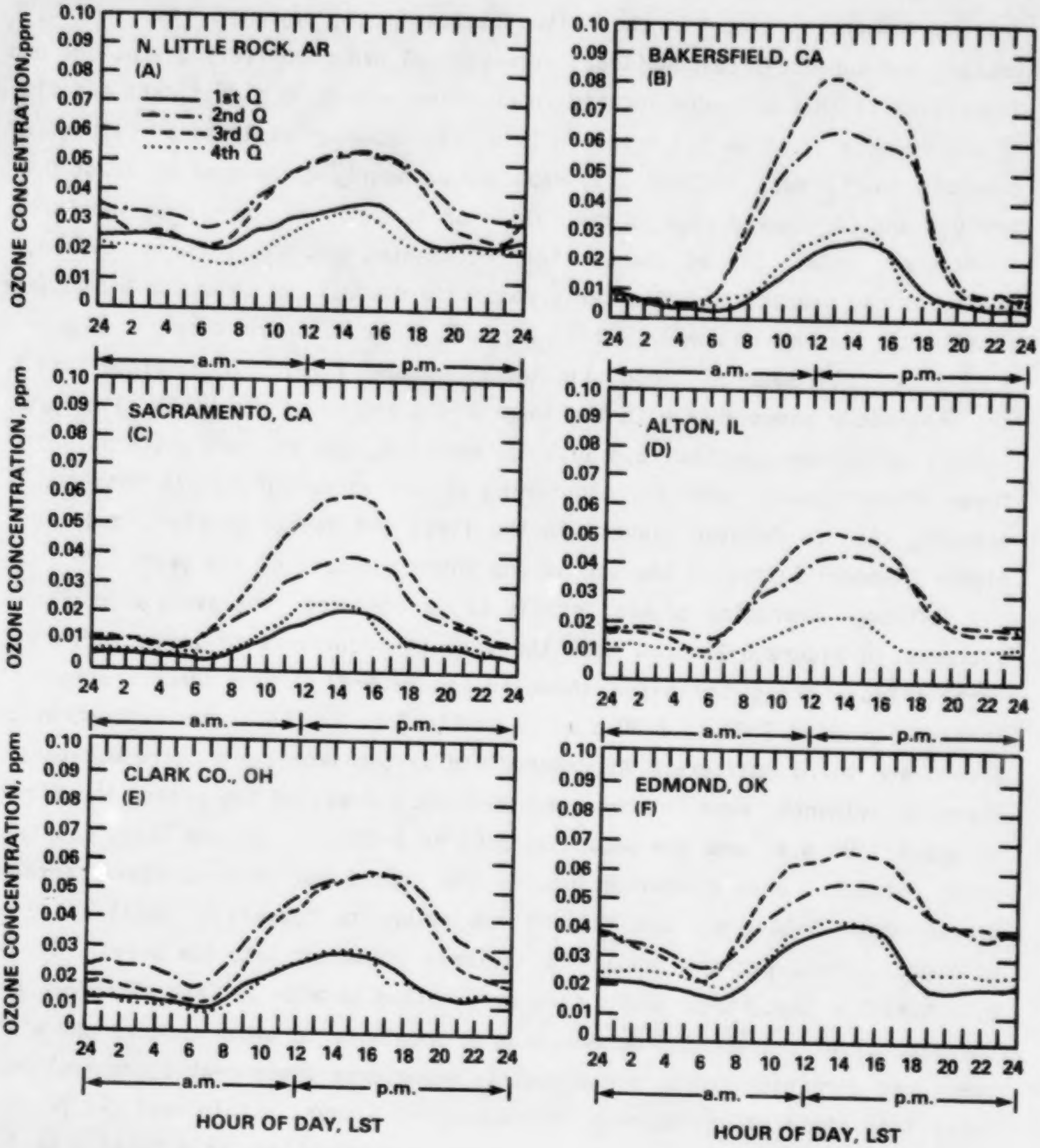

Figure 6-27 (A-F). Quarterly composite diurnal patterns of ozone concentrations at selected sites representing potential for exposure of major crops, 1981.

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

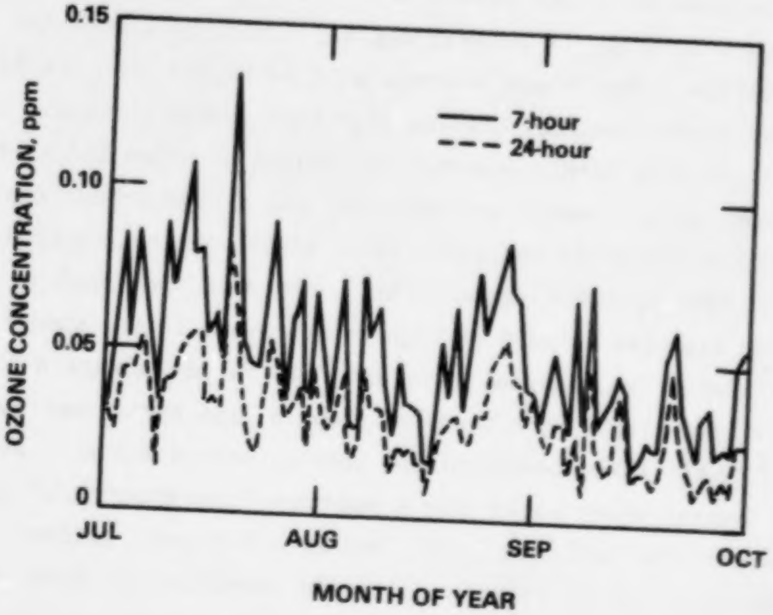

Figure 6-28. Daily 7-hour and 24-hour average ozone concentrations at a rural (NCLAN) site in Argonne, IL, 1980.

Source: Kress and Miller (1983)

at Argonne monitors ozone concentrations over a 7-hour daytime period approximating the period of peak photosynthesis in crops. The data in Figure 6-22 yield a 24-hour average ozone concentration of 0.026 ppm (Kress and Miller, 1983). The 7-hour average for the same 7-week period at the Argonne site is 0.042 ppm (Kress and Miller, 1983). The day-to-day variations in both the 7-hour and the 24-hour averages generally appear to be greater than the average difference within a day for either the 7-hour or 24-hour periods (Figure 6-22). The fluctuations in 1-hour values within a day or from day to day would be larger than within-day or between-day variations in either the 7-hour or the 24-hour average. The 7-hour average will be higher than the 24-hour average because the former excludes the low nighttime concentrations.

In Figure 6-29 (A-H), seasonal variations in ozone concentrations in 1981 are depicted using 1-month averages and the single 1-hour maximum concentration within the month for eight sites across the nation (U.S. Environmental Protection Agency, SAROAD data file). The data from most of these sites exhibit the expected pattern of high ozone levels in the summer and low levels in the winter. The seasonal rise and fall is not always a simple smooth curve, however. Tampa, for example, shows a late spring maximum. Dallas data also tend to be skewed toward higher spring concentrations. Averaging together data for several years would give a smoother "characteristic" pattern but also would obscure the fact that local, and even national, weather in a particular year plays at least as big a role in the formation of ozone as the regular seasonal changes in the elevation of the sun and the resulting variations in insolation. Because of seasonal changes in storm tracks from year to year, the general weather conditions in a given year may be more favorable for O_3/O_x formation than during the prior or following year. Thus, short-term concentration trends may not be indicative of real changes in air quality.

6.5.1.3 Weekday-Weekend Variations in Ozone Concentrations. Atmospheric ozone concentrations represent the combined effects of emission sources and meteorological conditions. The various sections of this document have been based on the assumption that the ozone precursor sources were operating in a generally steady state or at least on an average, repeatable diurnal cycle. For the most part, urban source patterns of oxidant precursors appear reasonably constant; however, in most urban areas there are decided changes that occur in traffic and commercial patterns that are keyed to a weekday-weekend activity cycle. The impacts of these changes have been observed in corresponding changes in ozone concentration patterns.

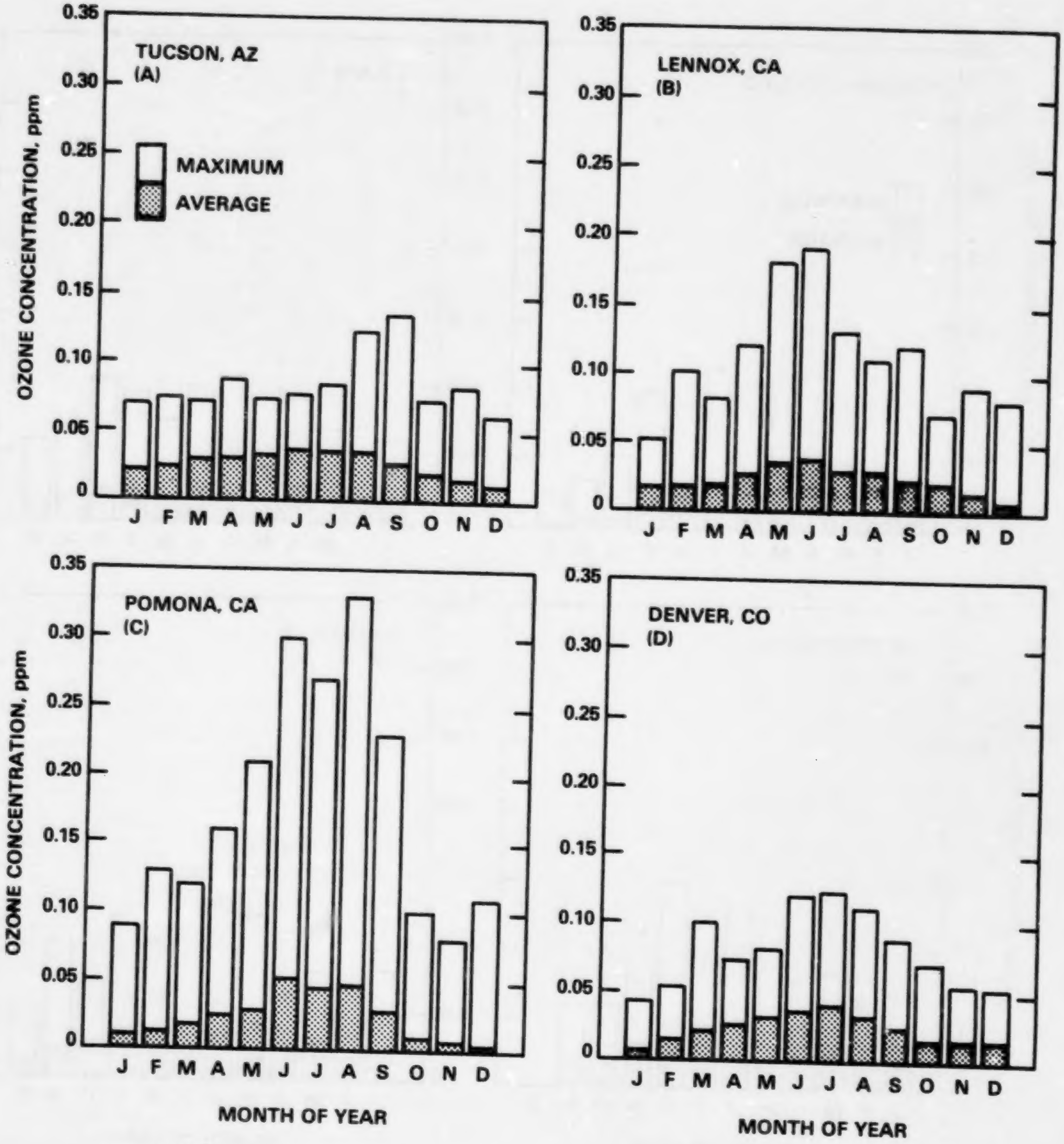

Figure 6-29 (A-H). Seasonal variations in ozone concentrations as indicated by monthly averages and the 1-hour maximum in each month at selected sites, 1981.

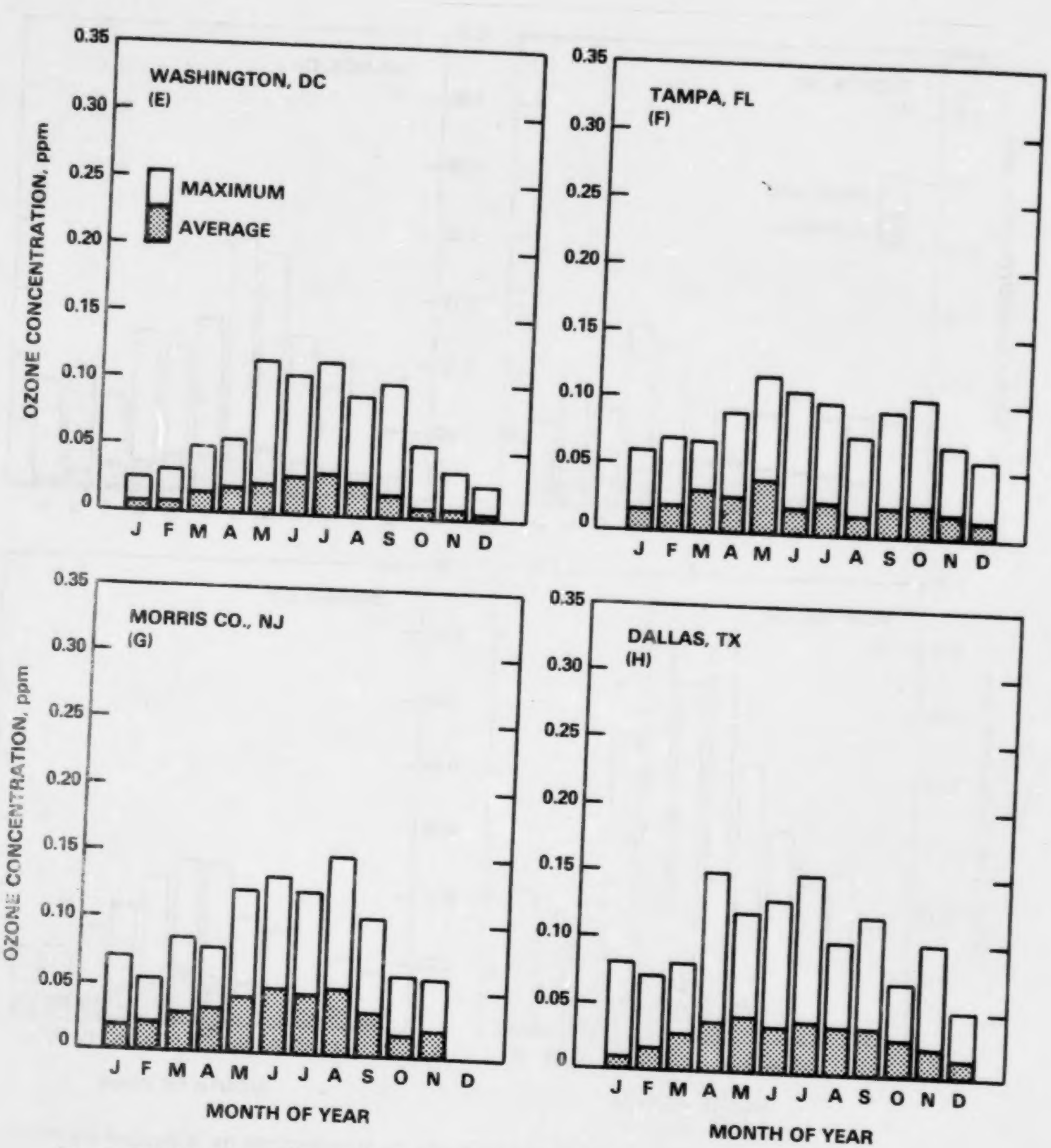

Figure 6-29 (A-H) (continued). Seasonal variations in ozone concentrations as indicated by monthly averages and the 1-hour maximum in each month at selected sites, 1981.

In an analysis of data from the 1960s in the Los Angeles basin, Schuck et al. (1966) noted a summertime shift in oxidant maximum values on the weekend from the central basin commercial and urban areas to suburban and coastal areas. These authors attributed this change to shifts in traffic pattern to recreational travel on the weekends. Other early analyses revealed no weekday/weekend difference in oxidant concentrations (as opposed to spatial shifts) and apparently none in the Los Angeles Basin, based on the observation that most alerts occurred on Friday and no alerts had ever occurred on Sunday (Altshuller, 1975).

Figures 6-30 through 6-32 show average hourly ozone concentrations for the summer months of July, August, and September, 1981, for Pomona and Lennox, California, and Little Rock, Arkansas, in which the data have been separated into Sundays and the other 6 weekdays. Data used in these figures are for 3 months only, but the Sunday patterns differ somewhat from weekday patterns in each of the months considered. For the most part, the Sunday daytime ozone concentrations are higher than the corresponding weekday concentrations, although these data are not definitive. In areas such as Little Rock, where even summertime ozone is close to typical background concentrations, as indicated by Figure 6-32, day-of-the-week shifts are less pronounced than in California.

The concentration cycles for ozone that appear to be related to Sunday/weekday changes are generally subtle, but they may have an influence on interpretations of urban and suburban exposures and other effects data.

6.5.2 Spatial Variations in Ozone Concentrations

Ozone is commonly thought of as a regional pollutant. Data abound to confirm that some urban regional airsheds have higher average ozone concentrations than others. In addition, an examination of specific sites within an airshed will also show that spatial variations in ozone concentrations occur to cause differing microscale exposures both of human populations within the same urban airshed and of crops and other vegetation in nonurban areas.

6.5.2.1 Urban versus Nonurban Variations. Data were presented in the 1978 document demonstrating that peak concentrations of ozone in rural areas are generally lower than those in urban areas, but that "dosages or average concentrations in rural areas are comparable to or even higher than those in urban areas" (U.S. Environmental Protection Agency, 1978). The diurnal concentration

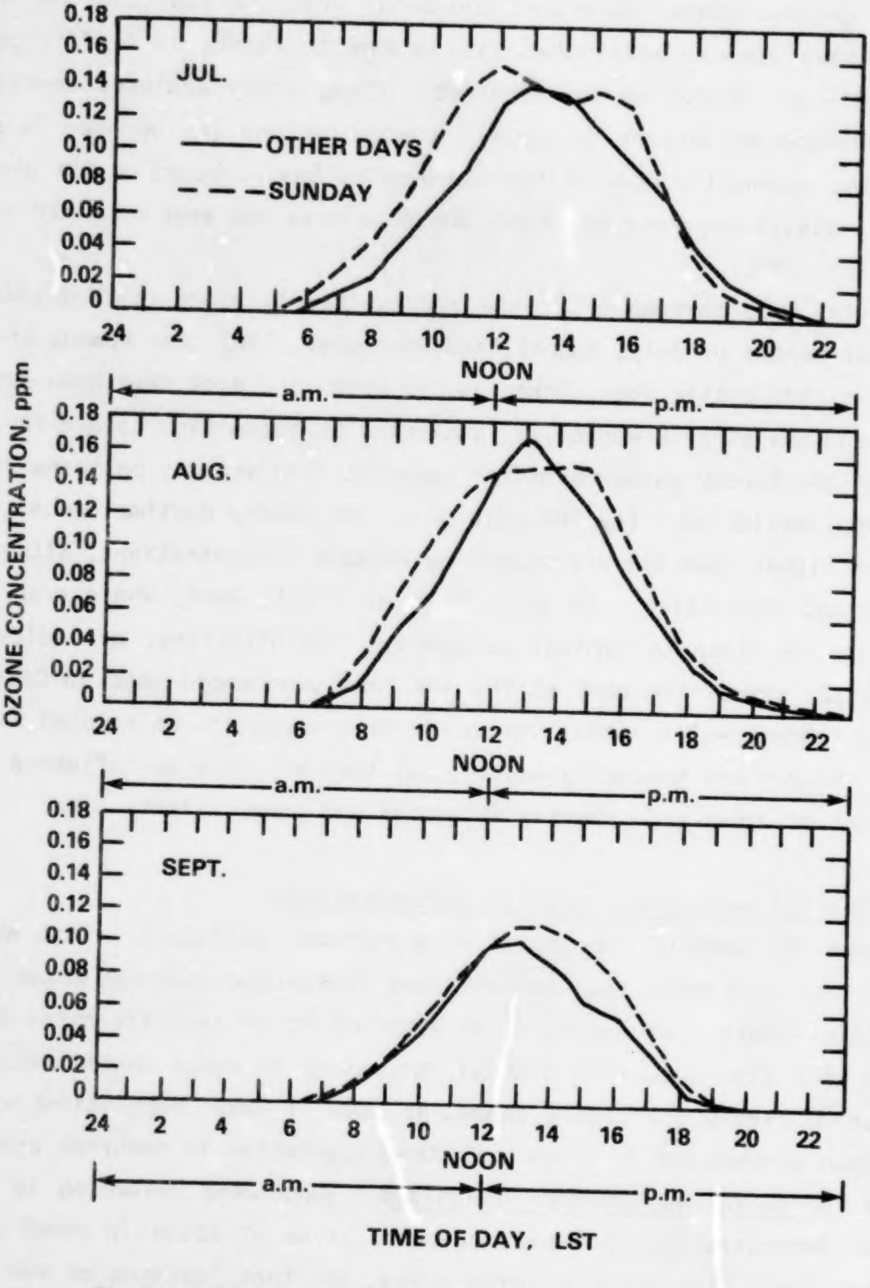

Figure 6-30. Composite diurnal data for Sunday versus other 6 days for July through September 1981, Pomona, CA.

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

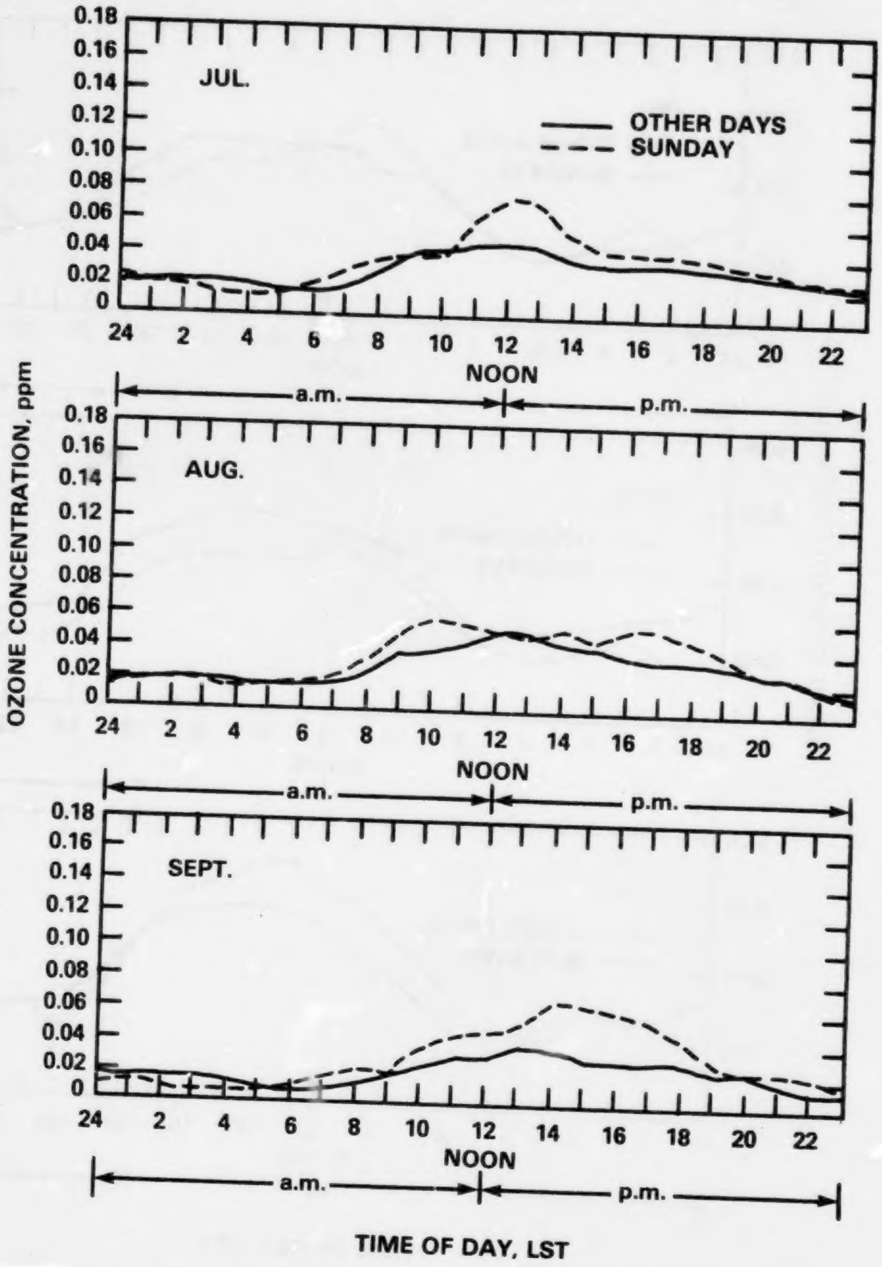

Figure 6-31. Composite diurnal data for Sunday versus other 6 days for July through September 1981, Lennox, CA.

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

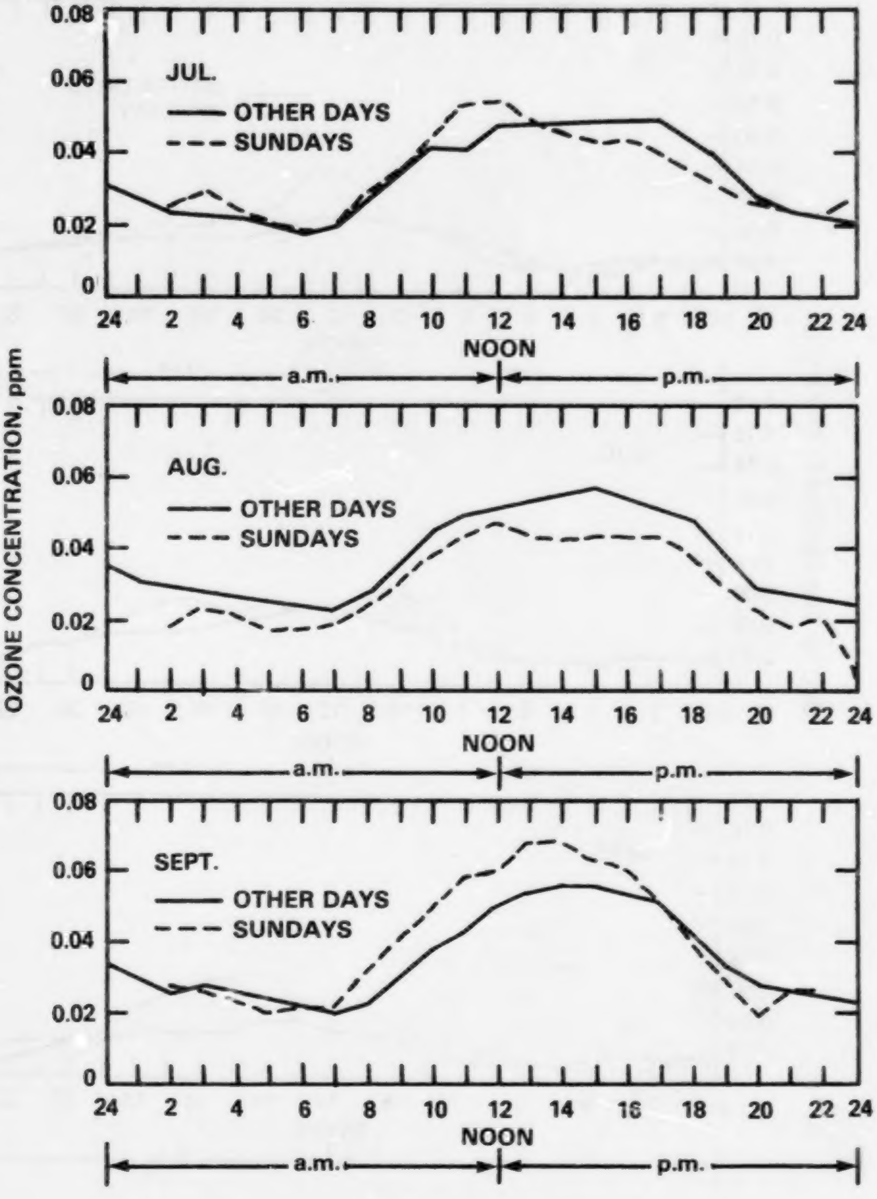

Figure 6-32. Composite diurnal data for Sunday versus other 6 days for July through September 1981, Little Rock, AR.

Source: U.S. Environmental Protection Agency, SAROAD data file for 1981

data presented in the preceding section indicate that peak ozone concentrations can occur later in the day in rural areas than in urban, with the distance downwind from urban centers generally determining in large measure how much later the peaks occur. The data presented in the preceding section for Montague, Massachusetts, in Figure 6-21 (Singh and Martinez, 1979) exemplify high late-afternoon secondary peak concentrations resulting from transport.

The NAPBN and other nonurban data in section 6.4 illustrate the typical urban-nonurban gradient that exists between peak ozone concentrations. While corroboration of the statement in the 1978 document that dosages and average concentrations in rural areas are higher than in urban areas would require calculations of means or ppm-hours, Figure 6-27 supports that conclusion. Ozone concentrations during nighttime and early-morning hours are lower in Bakersfield and Sacramento, California, than at the other four sites. Both areas represent crop-growing areas but both are essentially urban areas and are affected by other urban areas upwind. The other four sites are either suburban or rural. The lower nighttime and early-morning ozone concentrations found in urban areas are typically explained as resulting from ozone scavenging by reaction with nitric oxide.

Another consideration pertinent to potential exposures of crops in rural areas is the well-documented fact that ozone persists longer in nonurban than in urban areas (Coffey et al., 1977; Cleveland et al., 1976; Wolff et al., 1977; Isaksen et al., 1978). Again, the absence of chemical scavengers appears to be the chief reason.

6.5.2.2 Intracity Variations. Despite relative intraregional homogeneity, evidence exists for intracity variations in concentrations that are pertinent to potential exposures of human populations and to assessing actual exposures sustained in epidemiologic studies. Two illustrative pieces of data are presented in this section, one a case of relative homogeneity in a city with a population under 500,000 (New Haven, Connecticut) and one a case of relative inhomogeneity of concentrations in a city of greater than 9 million population (New York City) (U.S. Department of Commerce, 1982).

New Haven, Connecticut was the site of an epidemiological study in 1976 by Zagraniski et al. (1978). Symptoms recorded in subjects' diaries were correlated with ozone concentrations measured by the chemiluminescence method at a downtown New Haven site characterized as Center City-Residential. Table 6-11 shows several percentiles in the distribution of hourly values for

TABLE 6-11. OZONE CONCENTRATIONS AT SITES IN AND AROUND NEW HAVEN, CONNECTICUT, 1976 (CHEMILUMINESCENCE METHOD, HOURLY VALUES IN ppm)

Site (SAROAD No.)	No. Measurements	% of values ≤ stated concentration 50%	90%	95%	99%	Max Concn.
New Haven, CT: (070700123F01)	4119	0.021	0.035	0.091	0.162	0.274
Derby, CT: (070190123F01)	5698	0.023	0.038	0.071	0.095	0.290
Hamden, CT: (070400001F01)	3853	0.030	0.045	0.075	0.098	0.240

Source: U.S. Environmental Protection Agency, SAROAD data file for 1976.

that site plus two other sites in the county that were operating at the time, one in Derby, Connecticut, 9 miles west of New Haven, and one in Hamden, Connecticut, 6 miles north. The Derby site also is characterized as Center City-Commercial, the Hamden site as Rural-Agricultural. The general similarity of values among the three sites appears to substantiate the New Haven data used in the epidemiological study since there was probably a reasonable temporal correlation between these close sites. This shows that wherever study subjects might have traveled about the county, they probably incurred similar exposures to ambient ozone. This conclusion is reinforced by the data in Table 6-12, showing the date and time of the maximum hourly concentrations by quarter at these three sites. The significant data are those for the second and third quarters when the potential for O_3 formation and for exposure is the greatest. Differences in peak concentrations varied from 0.006 ppm in the fourth quarter to 0.055 ppm in the third quarter among sites.

The source of much of the ozone found in the New Haven, Connecticut, area is the greater New York City area (e.g., Cleveland et al., 1976) and an urban plume transported over considerable distance would tend to be relatively uniform

TABLE 6-12. QUARTERLY MAXIMUM 1-HOUR OZONE VALUES AT SITES IN AND AROUND NEW HAVEN, CONNECTICUT, 1976 (CHEMILUMINESCENCE METHOD, HOURLY VALUES IN ppm)

	Quarter of Year			
	1	2	3	4
New Haven, CT				
(No. measurements	10	1964	2079	66
Max 1-hr, ppm	0.045	0.274	0.235	0.066
(Hour of day)	11:00 a.m.	2:00 p.m.	2:00 p.m.	10:00 p.m.
Date	3/29	6/24	8/12	10/3
Derby, CT				
No. measurements	11	2140	2187	1360
Max 1-hr, ppm	0.015	0.280	0.290	0.060
(Hour of day)	11:00 p.m.	2:00 p.m.	2:00 p.m.	7:00 p.m.
Date	3/31	6/24	8/12	12/20
Hamden, CT				
No. measurements	56	2065	1446	286
Max 1-hr, ppm	0.050	0.240	0.240	0.065
(Hour of day)	Noon	3:00 p.m.	1:00 p.m.	3:00 p.m.
Date	3/29	6/24	7/20	10/7

Source: U.S. Environmental Protection Agency, SAROAD data file for 1976.

The highest or second-highest 1-hour maximum ozone concentration reported from a given station during a given year frequently gives an indication of the potential for repeated human exposure to high ozone levels. Nevertheless, a one-to-one correspondence between peak levels and either the number of days or the number of hours that a given level may be exceeded does not necessarily exist. Data obtained in the metropolitan New York area illustrate this latter fact (Smith, 1981). Data for 1980 are given in Table 6-13. These data were obtained at the monitoring sites shown in Figure 6-33. The second highest 1-hour ozone readings at the Eisenhower Park and Queens College stations have values only a few percentage points apart, yet there were 51 hours of ozone concentrations exceeding 0.12 ppm and 15 days when ozone levels exceeded 0.12 for at least 1 hour at the Queens College Station; whereas corresponding values were recorded at Eisenhower Park for only 7 hours during 2 days. At both stations, data for about 94 percent of possible hours were recorded as valid. Thus, the pattern of repeated peak exposures is different between these two stations, a fact having likely significance for health and welfare effects.

The range of first-, second-, third-, and fourth-highest values, along with frequencies of values >0.12 ppm, establishes an apparent concentration gradient in the area from sites 6 and 5 to site 4. Exposure of human populations living and working in metropolitan New York City could differ appreciably if the residences were located and all activities were centered in lower Brooklyn as opposed to the upper Bronx. Differences in peak concentrations at the respective sites varied by date (6/14 to 8/28); and by level on the same day (8/28), when ozone was 0.080 ppm at site 4 and 0.174 at site 7, a difference of 0.094 ppm.

6.5.2.3 Indoor-Outdoor Ozone Concentration Ratios. It has long been realized that most people in the United States spend a large proportion of their time indoors. Essentially all air pollution monitoring, however, is done on outdoor air. A knowledge of actual exposures of populations to ozone is essential for optimal interpretation and use of the results of epidemiological studies. The modeling of actual exposures, as opposed to potential exposures, necessitates knowing general activity patterns and at least approximate indoor/outdoor ratios (I/O) of ozone.

For slowly reacting compounds such as carbon monoxide, and in the absence of indoor sources, the long-term average ratios of the indoor to the outdoor concentration tends to be close to unity, although over short time periods the

I/O may be significantly different because of non-equilibrium factors (Yocom, 1982). In contrast, the situation for reactive pollutants such as ozone is much more complex, and reported I/O values for ozone are highly variable. Unfortunately, the number of experiments and kinds of structures examined

TABLE 6-13. PEAK OZONE CONCENTRATIONS AT EIGHT SITES IN NEW YORK CITY AND ADJACENT NASSAU COUNTY, 1980[a]

Site	Site no.	No. 1-hr averages >0.12 ppm	Days with 1-hr averages >0.12 ppm	Four highest daily values, ppm, and date			
				1st	2nd	3rd	4th
Susan Wagner H.S.	1	20	8	0.174 (8/28)	0.152 (7/18)	0.140 (7/26)	0.131 (9/1)
Mabel Dean H.S.	2	19	10	0.155 (7/21)	0.154 (7/26)	0.144 (7/18)	0.139 (8/28)
Woolsey Post Office	3	37	6	0.188 (7/20)	0.163 (7/21)	0.151 (7/22)	0.148 (8/28)
Mamaroneck	4	0	0	0.092 (6/14)	0.080 (8/28)	0.076 (7/2)	0.075 (7/26)
P.S. 321	5	24	9	0.148 (7/26)	0.146 (8/28)	0.165 (7/18)	0.145 (7/9)
Sheepshead Bay H.S.	6	44	12	0.184 (7/31)	0.173 (7/18)	0.165 (8/7)	0.164 (7/14)
Queens College	7	51	15	0.174 (8/28)	0.164 (7/21)	0.163 (6/14)	0.159 (8/24)
Eisenhower Park	8	7	2	0.175 (8/28)	0.158 (7/21)	0.119 (7/20)	0.118 (8/24)

[a] Sites monitored during the Northeast Corridor Monitoring Program (NECRMP); site numbers assigned here are keyed to Figure 6-33. For NECRMP site numbers, see Smith (1980).

Source: Smith (1981)

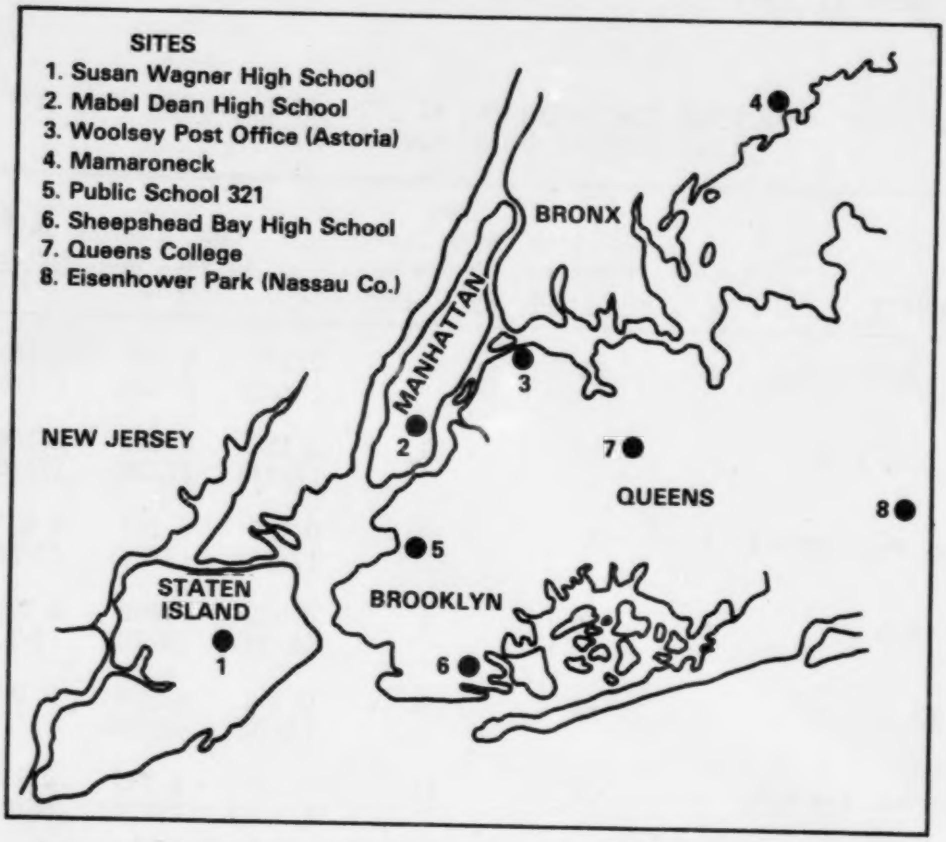
SITES
1. Susan Wagner High School
2. Mabel Dean High School
3. Woolsey Post Office (Astoria)
4. Mamaroneck
5. Public School 321
6. Sheepshead Bay High School
7. Queens College
8. Eisenhower Park (Nassau Co.)
BRONX
MANHATTAN
NEW JERSEY
QUEENS
STATEN ISLAND
BROOKLYN
1
2
3
4
5
6
7
8

Figure 6-33. New York State air monitoring sites for Northeast Corridor Monitoring Program (NECRMP).

Source: Smith (1981)

provide only limited data for use in modeling indoor exposures. Yocom (1982) has presented a chronological summary of studies in which either ozone or photochemical oxidant indoor-outdoor gradients were measured. Studies have been conducted over the period 1971 through the present (one ongoing study) by five research organizations: University of California, the California Institute of Technology, GEOMET, Inc., Lawrence Berkeley Laboratory, and TRC Environmental Consultants. Structures examined have included hospitals, schools, office buildings, single-dwelling homes, "experimental" dwellings, apartments, and mobile homes. Private homes included those with and without gas stoves and fireplaces, and those inhabited by smokers versus nonsmokers. Areas of the country in which the buildings were located ranged from Southern California to Boston, including as well, Denver, Chicago, Washington, D.C., Baltimore, Pittsburgh, and other unspecified locations (Yocom, 1982).

The results of a number of the studies conducted to determine I/O for ozone in a variety of building types are shown in Table 6-14. These results are highly variable, to say the least. The variability is not surprising, considering the diversity of structures and locations included in the studies. In this tabulation the highest I/O value of 0.80 was reported by Sabersky et al. (1973) on the basis of smog-season measurements in a multistory, air-conditioned building on the Pasadena campus of the California Institute of Technology. Air exchange in this building was at a rate of 10 changes per hour with 100 percent outside air (i.e., no recirculation of inside air). For another Cal Tech building, in which there was a mix of 70 percent outside air and 30 percent recirculated inside air, Sabersky et al. (1973) found an indoor-outdoor ozone ratio of 0.65. The lowest indoor-outdoor ozone concentration ratios shown in Table 6-14 are those reported by Berk et al. (1981), which were in the range of 0.10 to 0.25. These data were the result of studies in energy-efficient housing, where ventilation was restricted in various ways for energy conservation. These experiments were carried out in Medford, Oregon. The research of Moschandreas et al. (1978, 1981) was carried out on east-coast residences and those results were also highly variable.

A relatively large number of factors can affect the difference in ozone concentrations between the inside of a structure and the outside air. In general, outside air infiltration or exchange rates, interior air circulation rates, and interior surface composition (e.g., rugs, draperies, furniture) affect the balance between replenishment and decomposition of ozone within buildings (Thompson et al., 1973; Sabersky et al., 1973; Berk et al., 1980;

TABLE 6-14. SUMMARY OF REPORTED INDOOR-OUTDOOR OZONE RATIOS

Structure	Indoor-outdoor ratio (I/O)	Reference
Residence (with evaporative cooler)	0.60[a]	Thompson et al. (1973)
Office (air-conditioned; 100% outside air intake)	0.80 ± 0.10	Sabersky et al. (1973)
(air-conditioned; 70% outside air intake)	0.65 ± 0.10	
Residence	0.70	
Residence	0.50 to 0.70	Moschandreas et al. (1978)
Residence (gas stoves)	0.19	Moschandreas et al. (1981)
(all electric)	0.20	
Office	0.29	
School room	0.19 (max)	Berk et al. (1980)
Residence	0.10 to 0.25	Berk et al. (1981)

[a] Measured as total oxidants.

Moschandreas et al., 1978). The rate at which exterior air enters a building depends on local wind speed and direction, on how well-sealed the building is, on how frequently doors and windows are opened, and on the operating characteristics and cycles of heating/air conditioning/ventilating systems. A significant factor that increases infiltration is an increasing temperature differential between warm interior air and cold outside air (Moschandreas et al., 1978), although such a differential would be unusual for a photochemical smog period. Moschandreas et al. (1978) reported exterior-interior exchange rates ranging from ten changes per hour in an office building to one change every 5 hours in a residence. At the higher exchange rates, inducted ozone remains at a level indoors that is closer to the outdoor level. As the exchange rate decreases, surface decomposition processes can result in progressively lower equilibrium ozone concentrations. Other factors, such as relative humidity, also affect decomposition. The half-life of ozone inside residences has been estimated at 2 to 6 minutes (Moschandreas et al., 1978; Mueller et al., 1973; Sabersky et al., 1973), while its half-life in an office environment has been estimated at 11 minutes (Mueller et al., 1973). These results are indicative of the relatively rapid reaction rate that can be expected for ozone in a building or room environment. The problem of I/O values in buildings was the subject of a model development program by Shair and Heitner (1974) in which they tried to account for ventilation and for losses by reactions and surface scavenging. Considering the research results shown in Table 6-13 and summarized by Yocom (1982), any estimates of indoor ozone exposures to occupants must be considered as having a large degree of probable variability.

At present there are no long-term monitoring data on indoor air pollutant concentrations that are comparable to the concentration or exposure patterns that are available for outdoor locations. Thus, for estimates of the exposure of building occupants to ozone and other photochemical oxidants, it is necessary to rely on extrapolations of very limited I/O data such as those shown in Table 6-13.

6.5.2.4 Macroscale Variations in Ozone Concentrations: Effects of Altitude and Latitude. The 1978 criteria document presented discussions on the effects of tropopause-folding events (TF), and of the seasonal tropopause adjustment (STA) and small-scale eddy transport (SSET) mechanisms on stratospheric-tropospheric exchange. As described previously in chapter 4, TF events would be expected to produce rare increases in ground-level ozone concentrations, resulting from strong incursions of stratospheric ozone, in the southern and eastern United States (latitudes of about 37°N and less and longitudes of about 90° and less) (U.S. Environmental Protection Agency, 1978). The STA and TF mechanisms result in stratospheric-tropospheric interchange in the same season (winter or winter-to-spring) and in the same latitudes.

Concentrations of ozone can be expected to vary with altitude and with latitude. These variations occur because of the interchange mechanisms involved in stratospheric-tropospheric exchange, the decay of stratospheric ozone as it traverses the troposphere, and the known production in the apparently unpolluted troposphere of ozone at certain altitude ranges above mean sea level (MSL). Seiler and Fishman (1981) reported on ozone measurements taken on flights in remote tropospheric air during July and August 1974. Averages of their data show that ozone concentrations increase with increasing altitude and in general substantiate the accepted belief that the earth's surface and the lower atmosphere act as ozone sinks. The value for the average ozone concentration in the troposphere is about 0.035 ppm ± 30 percent. Tropospheric ozone shows a marked hemispheric asymmetry; the higher concentrations occur in the northern hemisphere.

Logan et al. (1981) summarized earlier measurements of background tropospheric ozone. Hemispheric asymmetry is readily apparent in their results, as is the seasonal increase in lower tropospheric ozone in the summer at mid-latitudes in the northern hemisphere.

6.5.2.5 Microscale Variations in Ozone Concentrations: Effects of Monitor Placement. Just as macroscale variations in ozone concentrations have been observed by measuring vertical and horizontal profiles at various altitudes, so too have microscale variations been observed as a function of placement of sampling probes.

Data drawn from a recent study on rural ozone concentrations illustrate the possible effects of sampling probe location on the resulting concentration data. The data given here illustrate lesser-known effects of placement of monitoring probes that are pertinent for vegetation studies, in particular.

Pratt et al. (1983) studied concentrations of ozone and oxides of nitrogen in the upper-midwestern part of the United States. Concentration data were obtained over 4 years by means of monitors at two sampling heights (ca. 3 and 9 meters) at three air quality monitoring sites: LaMoure County, North Dakota; Traverse County, Minnesota; and Wright County, Minnesota. All stations were rural sites. The mean O_3 concentrations did not differ greatly among the sites, but in at least some instances the mean differences between sampling heights were as large or larger than the differences among the scattered sites. Table 6-15 presents the mean ozone concentrations measured at two separate sampling heights (Pratt et al., 1983). Annual average concentrations were 1 to 3 ppb lower at the 3.05-meter height than at the 6.10 and 9.14-meter heights, reflecting the depletion of ozone near the surface. As might be expected, the gradient was especially conspicuous at night because of the continued surface scavenging and a decrease in the rate of transfer from layers aloft. The concentrations of ozone occuring at these sites were near background in all years measured. In areas with higher ozone concentrations, one would expect to see larger absolute gradients between monitors at different heights. In fact, the careful measurement of concentration gradients over distances of 1 to 10 meters is a recognized method for estimating the scavenging potential of a surface.

6.6 CONCENTRATIONS OF PEROXYACETYL NITRATE (PAN) AND PEROXYPROPIONYL NITRATE (PPN) IN AMBIENT AIR

6.6.1 Introduction

As noted in the introduction to this chapter (section 6.1), published data on the concentrations in ambient air of photochemical oxidants other than ozone are not comprehensive or abundant. Much more is known now, however, about their atmospheric concentrations than was known when the 1978 criteria document for ozone and other photochemical oxidants was published. Review of the data that follow will show that peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and hydrogen peroxide (H_2O_2) are the most abundant of the non-ozone oxidants in ambient air in the United States other than the inorganic nitrogenous oxidants such as nitrogen dioxide (NO_2) and possibly nitric acid (HNO_3), in some areas. The inorganic nitrogenous oxidants found in ambient air are reviewed in air quality criteria documents on the nitrogen oxides and are not treated in this document except for the review of the role of nitric oxide (NO) and NO_2 in atmospheric photochemistry.

In this section, the concentrations of PAN and PPN in ambient air will be presented in order to examine potential exposures to these oxidants of human populations, vegetation, and terrestrial ecosystems.

TABLE 6-15. MEANS AND STANDARD ERRORS OF OZONE CONCENTRATIONS MEASURED OVER 4 YEARS AT TWO SAMPLING HEIGHTS AT THREE STATIONS IN THE RURAL, UPPER-MIDWESTERN UNITED STATES (ppb/v/v)

Site	Sampling height, m	Years 1977	1978	1979	1980	1981	1977-1981
LaMoure County, ND	3.05	22.97 ± 0.20 (6,413)[a]	35.30 ± 0.20 (15,218)	30.80 ± 0.16 (21,064)	34.98 ± 0.25 (17,157)	31.92 ± 0.26 (6,699)	32.26 (66,551)
	9.14	24.14 ± 0.19 (6,410)	35.67 ± 0.19 (15,220)	32.25 ± 0.15 (20,470)	37.53 ± 0.25 (17,157)	34.23 ± 0.26 (6,364)	33.82 65,597
Traverse County, MN	3.05	24.44 ± 0.19 (9,672)	35.2 ± 0.19 (22,675)	30.64 ± 0.17 (19,900)	34.66 ± 0.23 (22,629)	28.78 ± 0.23 (7,141)	32.09 (82,017)
	9.14	26.29 ± 0.19 (9,810)	36.77 ± 0.19 (22,624)	32.39 ± 0.16 (19,289)	37.60 ± 0.23 (22,625)	31.08 ± 0.22 (7,142)	34.21 (81,550)
Wright County, MN	3.05	-	34.64 ± 0.23 (17,437)	28.71 ± 0.18 (17,771)	34.27 ± 0.26 (18,222)	31.60 ± 0.24 (7,764)	32.42 (61,254)
	6.10	-	35.61 ± 0.23 (17,440)	29.27 ± 0.18 (17,775)	35.16 ± 0.27 (18,280)	32.28 ± 0.24 (7,766)	33.21 (61,261)

[a] The numbers in parentheses refer to the number of hours of monitoring included in the reported values. Values are based on all valid data per site. For each sampling height at each site, values for three monitors separated by 76 m are included in the calculations. Monitoring was conducted only during the second half of 1977 and only until 30 June in 1981.

Source: Pratt et al. (1983)

No data indicating potentially adverse effects of PPN are available. It exists in trace quantities and apparently no research has ever been undertaken to determine potential toxicity. At least one study (Heuss and Glasson, 1968) has reported that peroxybenzoyl nitrate (PBzN), like PAN, is a lachrymator. No unambiguous identification of PBzN in the ambient air of the United States has been made, however.

A number of facts about the toxicity and behavior of PAN are available, however, and are pertinent to the examination of its concentrations in ambient air:

1. On a concentration basis, PAN appears to be more phytotoxic than ozone (chapter 7). Although data on the health effects of PAN are sparse, PAN appears to be less toxic than ozone in animals and man (chapters 10 and 11).
2. As with ozone, PAN apparently has to enter the leaf of the plant to exert its toxic effects (chapter 7). Thus, to manifest its toxicity in plants, PAN has to be present when the stomata of the leaves are open, which is thought to be limited to the daylight photoperiod. Important in this context is the fact that no visible injury to plants from PAN will occur unless light is present before, during, and after exposure to PAN. This not true for ozone injury. Like ozone, however, PAN is more toxic to herbaceous (e.g., crops) than to woody vegetation (e.g., shrubs) (chapter 7).
3. Although PAN and ozone are individually toxic to man, animals, and vegetation, data on possible interactive effects are quite limited. In vegetation studies, higher concentrations of the combined pollutants produce effects that are less than additive; that is, the pollutants appear to be antagonistic (chapter 7).
4. Adsorption of PAN on reactive surfaces differs from that of ozone. Deposition velocities for PAN on vegetation may be as much as three times lower than for ozone (Hill and Chamberlain, 1976; in McMahon and Denison, 1979). Deposition velocities for soils may be greater for PAN, but velocities depend on type of soil and amount of soil water. More PAN is taken up by moist soil than by dry (Garland and Penkett, 1976), but more ozone is taken up by dry soil than moist (Garland, 1977).
5. No indoor PAN concentrations appear in the recent literature, but given the known deposition velocities for the respective pollutants, indoor/outdoor ratios for PAN may be higher than those of ozone. The persistence of PAN is thermally dependent, which also would influence indoor concentrations.

6. Nitric oxide (NO) does not scavenge PAN as effectively as it does ozone (U.S. Environmental Protection Agency, 1978); but NO may serve as a PAN scavenger when NO is at higher concentrations in the evening.

7. No damage to nonbiological materials has ever been attributed to PAN, singly or in combination with other pollutants. Apparently no research has been done in this area.

Given the above information about PAN, it is apparent that the concentrations of PAN that are of most concern are those in nonurban areas during daylight hours, relative to vegetation, and those both indoors and outdoors at all times in both urban and nonurban areas, relative to human populations. Since concentrations of precursors to PAN are lower in nonurban areas, whether PAN can, like ozone, be transported from urban areas is a major determinant of the levels likely to be found in nonurban (agricultural) areas. Most of the available data on concentrations of PAN in ambient air are from urban areas. This section presents historical and recent data on the concentrations of PAN and, where available, on PPN and on the patterns those concentrations assume.

6.6.2 Historical Data

In the 1970 criteria document for photochemical oxidants (U.S. Department of Health, Education, and Welfare, 1970), concentrations for total oxidants and PAN were reported for Los Angeles and Riverside, California. In Los Angeles, composite diurnal data for PAN (obtained by GC-ECD) showed average peak 1-hr concentrations of about 40 ppb in September 1965 and about 60 ppb in October 1965. The September peaks occurred around noon and the October peaks occurred shortly after 1:00 p.m., with the difference in time possibly being a function of the temperature-dependence of PAN formation and persistence. In Riverside, two peak concentrations were observed in composite diurnal data, one of $\gtrsim$ 4 ppb around 10:00 a.m. and one ~10 ppb between 4:00 and 6:00 p.m. Seasonal data from Riverside for June 1966 to June 1967 showed that PAN concentrations were highest in September 1966 and in March and June 1967.

Total oxidants (by Mast meter) in these Los Angeles sites reached a peak concentration (the same composite diurnal data as above) of close to 140 ppb in September 1965 at about the same hour of day as the PAN peak. In October, total oxidants peaked at nearly 200 ppb, again coinciding in time with peak PAN concentrations. In Riverside, the morning PAN peak preceded the ozone peak (~110 ppb around noon) by almost 2 hours but the afternoon PAN peak trailed the afternoon ozone peak (~160 ppb around 2:00 to 4:00 p.m.) by about 2 hours. The ozone/PAN ratio was lower from October until March than during the rest of the year.

In the 1978 criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1978), additional PAN data for Los Angeles as well as two other cities were presented. Lonneman et al. (1976) measured PAN and total oxidants in Los Angeles in 1968. In 118 samples collected for the period 10:00 a.m. to 4:00 p.m. during the study, the median PAN concentration was 13 ppb and the average PAN concentration was 18 ppb. The median total oxidant concentration (measured by UKI) was 97 ppb and the average was 117 ppb. Thus, the median oxidant/PAN ratio was 7.5 and the average oxidant/PAN ratio was 6.5.

Lonneman et al. (1976) conducted similar studies in Hoboken, New Jersey, in 1970 and in St. Louis, Missouri, in 1973. Samples were measured during the period 10:00 a.m. to 4:00 p.m. over the course of the study. In Hoboken, PAN concentrations averaged 3.7 ppb. Ozone concentrations (measured by chemiluminescence) averaged 90.5 ppb. In St. Louis, PAN averaged 6.4 ppb, ozone (measured by chemiluminescence) averaged 50.1 ppb, and total oxidants (by UKI) averaged 74.3 ppb.

From these 1966 through 1973 urban data, it is clear that PAN concentrations in urban areas are appreciably lower than those of ozone, even in the winter in California, when PAN concentrations are proportionally higher than those of ozone.

In addition to urban data, the 1978 criteria document (U.S. Environmental Protection Agency, 1978) also included PAN concentrations from one nonurban-agricultural area, Wilmington, Ohio (Lonneman et al., 1976). The maximum PAN concentration observed in 1500 samples taken during August 1974 was 4.1 ppb. The daily maximum PAN concentration rarely exceeded 3.0 ppb even though the daily maximum ozone concentration frequently exceeded 80 ppb.

Conclusions reached in the 1978 document were (1) that PAN concentrations are much lower in the ambient air of nonurban than of urban areas; and (2) that ozone/PAN or total oxidant/PAN ratios vary with location, such ratios being higher in nonurban areas than in urban (U.S. Environmental Protection Agency, 1978). From data presented in the 1970 document, it may be concluded (1) that oxidant/PAN ratios vary with season; (2) that PAN concentrations are lower than ozone concentrations in urban areas; and (3) that PAN and ozone concentrations exhibit similar but not identical diurnal patterns.

The historical data presented above have been given in some detail because the information about PAN conveyed by those data remains valid. Examination of the more recent data presented in subsequent sections shows that the newer data, for the most part, extend and corroborate the findings of the older literature.

6.6.3 Ambient Air Concentrations of PAN and Its Homologues in Urban Areas

Additional studies on concentrations of PAN and its homologues in both urban and nonurban areas are now available. Newer data have been summarized here, where possible, and the individual studies or examples presented are merely a few of many, chosen to represent current knowledge regarding ambient air PAN concentrations and their patterns.

The existing literature on the concentrations in ambient air of the peroxyacyl nitrates, PAN and its higher homologues, has been compiled and examined in two recent review articles (Temple and Taylor, 1983; Altshuller, 1983). In the first, Temple and Taylor reviewed the concentrations of PAN in the ambient air in Europe, Japan, and North America in the context of the phytotoxicity of PAN. Altshuller, in the second, reviewed the published concentrations of PAN and of PPN in ambient air, also within and outside the United States. In addition, Altshuller analyzed the relationships to ozone of PAN and other photochemical reaction products. The reader is referred to these reviews for detailed information and for references therein. The review by Altshuller (1983) is especially comprehensive.

Table 6-16 presents a summary of PAN concentrations observed in the ambient air of urban areas of the United States. Data in this table include the results of studies cited in section 6.6.2 as well as the results of newer studies. This table was derived from the reviews of Altshuller (1983) and Temple and Taylor (1983), as well as from a few additional sources (Jorgen et al., 1978; Lewis et al., 1983). The data are summarized in the table by region of the United States and by date, with the newer studies reported first for each region.

Because of variations in diurnal patterns of PAN by location and season, and because no national, uniform aerometric data base for PAN exists, few of the data reported in Table 6-16 are really comparable. Thus, data in this

TABLE 6-16. SUMMARY OF CONCENTRATIONS OF PEROXYACETYL NITRATE IN AMBIENT AIR IN URBAN AREAS OF THE UNITED STATES

Site	Time of yr	Yr	Hours sampled	No. days sampled	PAN concentrations, ppb				Original reference	Source[b]
					Method[a]	Avg.	Max.[b]	Monthly mean[b]		
West										
Riverside, CA	All year	1980	8 a.m.-8 p.m.	365	GC-ECD	-[c]	41.6	4.9	Temple and Taylor (1983)	Ref. 1
W. Los Angeles, CA	June	1980	6:35 a.m.-1:35 p.m.	2	LP-FTIR	7	16	-	Hanst et al. (1982)	Ref. 2
Claremont, CA	Sept.-Oct.	1980	24 hr/day	11	GC-ECD	13	47	-	Grosjean and Kok (1981)	Ref. 2
Claremont, CA	Aug.-Sept.	1979	Morning to late evening	8	GC-ECD	4	11	-	Tuazon et al. (1981a)	Ref. 2
Claremont, CA	Oct.	1978	Late morning to late evening	5	LP-FTIR	6	11	-	Tuazon et al. (1981a; 1981b)	Ref. 2
Riverside, CA	Apr., May	1977	24 hr/day	10	GC-ECD	1.6	5.7	-	Singh et al. (1979)	Ref. 2
Riverside, CA	July, Aug., Oct.	1977	Late morning to evening	10	LP-FTIR	7	18	-	Tuazon et al. (1980)	Ref. 2
Riverside, CA	All year	1975 (May)- 1976 (Oct.)	24 hr/day	533	GC-ECD	3.6	32	-	Pitts and Grosjean (1979)	Ref. 2
Riverside, CA	Oct.	1976	Late morning to early evening	3	LP-FTIR	9	18	-	Tuazon et al. (1978)	Ref. 2
West Covina, CA	Aug., Sept.	1977	23 hr/day	24	GC-ECD	9	20	-	Spicer (1977)	Ref. 2
West Covina, CA	Aug., Sept.	1973	NA[d]	NA	NA	-	46	8.8	Spicer (1974)	Ref. 1
Pasadena, CA	July	1973	7 a.m.-4:30 p.m.	3	LP-FTIR	30	53	-	Hanst et al. (1975)	Ref. 2
Riverside, CA	Aug.-Apr.	1967-1968	24 hr/day	273	GC-ECD	-	58	4.6	Taylor (1969)	Ref. 1
Downtown Los Angeles, CA	Sept.-Nov.	1968	10 a.m.-4 p.m.	-	GC-ECD	8	68	-	Lonneman et al. (1976)	Ref. 2

TABLE 6-16. SUMMARY OF CONCENTRATIONS OF PEROXYACETYL NITRATE IN AMBIENT AIR IN URBAN AREAS OF THE UNITED STATES (continued)

Site	Time of yr	Yr	Hours sampled	No. days sampled	PAN concentrations, ppb				Original reference	Source[b]
					Method[a]	Avg.	Max.[b]	Monthly mean[b]		
Salt Lake City, UT	July-Sept.	1966	7 a.m.-3 p.m.	-	GC-ECD	-	54	4.4	Tingey and Hill (1968)	Ref. 1
Los Angeles, CA	Sept.-Oct.	1965	8 a.m.-1 p.m.	35	GC-ECD	31	214	38 (Sept.) 40 (Oct.)	Mayrsohn and Brooks (1965)	Ref 1; ref. 2
Downtown Los Angeles, CA	July-Oct.	1960	9 a.m.-Noon	9	IR	~20	70	-	Renzetti and Bryan (1961)	Ref. 2
Southwest Houston, TX	Oct.	1977	8 a.m.-8 p.m.	-	GC-ECD	-	15.6	-	Jorgen et al. (1978)	Jorgen et al. (1978)
Houston, TX	July	1976	24 hr/day	22	GC-ECD	0.4	11.5	-	Westberg et al. (1978)	Ref. 2
Midwest Dayton, OH (Huber Heights, OH)	July, Aug.	1974	24 hr/day	20	GC-ECD	0.7	10	-	Spicer et al. (1976)	Ref. 1
St. Louis, MO	June-Aug.	1973	23 hr/day	26	GC-ECD	1.8	19	-	Spicer (1974)	Ref. 1; ref. 2
St. Louis, MO	Aug.	1973	8 to 24 hr/day	12	GC-ECD	6.3	25	-	Lonneman et al. (1976)	Ref. 1
East New Brunswick, NJ	All year	1978 (Sept.) -1980 (May)	24 hr/day (9600 1-hr values)	400	GC-ECD	0.5	10.6	-	Lewis et al. (1983)	Lewis et al (1983)
New Brunswick, NJ[e]	Sept.-Dec.	1978	8 a.m.-6 p.m.		GC-ECD	-	10.5	2.7	Brennan (1979)	Ref. 2
Hoboken, NJ	June, July	1970	10 a.m.-4 p.m.		GC-ECD	-	9.9	3.7	Lonneman et al. (1976)	Ref. 2

[a] GC-ECD, gas chromatography with electron-capture detector; LP-FTIR, long-path Fourier-transform infrared spectroscopy; IR, infrared spectroscopy.

[b] Reference 1 is Altshuller (1983); reference 2 is Temple and Taylor (1983).

[c] Ref. 1 reported averages for the sampling period; reference 2 reported monthly means.

[d] Not available.

[e] Subset of data reported by Lewis et al. (1983), cited in table above.

table lend themselves to general conclusions but not to the analysis of trends over the past decade and a half or necessarily to analysis of between-city or between-region similarities or differences. Concentrations of PAN in Los Angeles in 1965 appear to have been a great deal higher (Mayrsohn and Brooks, 1965) than in 1980 (Hanst et al., 1982) for nearly the same time of day, but the 1965 concentrations were measured in September and October and the 1980 concentrations were measured in June. Other data from California indicate that September and October are more likely to be part of the smog season there than June. A comparison of PAN concentrations in Riverside in 1980 with those in 1967 and 1968 indicates little difference. Again, however, the sampling periods were not identical relative to averaging time or time of year.

In their review, Temple and Taylor (1983) have presented monthly average PAN concentrations for 1967-1968 and for 1980. These data are plotted in Figure 6-34, derived from their tabular data. More similarities than differences are apparent.

In addition to compiling existing data on the concentrations of PAN in ambient air, Altshuller (1983) also did the more difficult task of relating PAN concentrations to ozone concentrations where data for both exist. It must be borne in mind that sampling periods (years, time of year, number of measurements) are not identical and in many cases are not even similar (see Table 6-16). Neither are the averaging times over which samples were collected and calculated within respective studies identical or even necessarily similar. Nevertheless, the data of Altshuller constitute a comprehensive review and examination of the relationships among respective photochemical oxidants in urban areas of the United States. For ease of presentation, PAN/O_3 ratios, expressed as percentages, are given in Table 6-17, but Table 6-16 should be consulted for information on sampling periods and averaging times.

The existence of peroxybenzoyl nitrate (PbzN) in ambient air of urban areas was postulated in the 1978 criteria document for ozone and other oxidants (U.S. Environmental Protection Agency, 1978). Although it has been reported to occur in ambient air in Europe, PBzN has not been clearly identified in ambient air in the United States. Hanst et al. (1982) estimated that 2 ppb PBzN would be clearly discernible in FTIR measurements but reported no clear absorption band for PBzN in their measurements during a smoggy period in Los Angeles. They estimated an upper limit of 1 ppb PBzN during their 1980 study (the maximum ozone concentration was 272 ppb and the maximum PAN concentration was 16 ppb during that period).

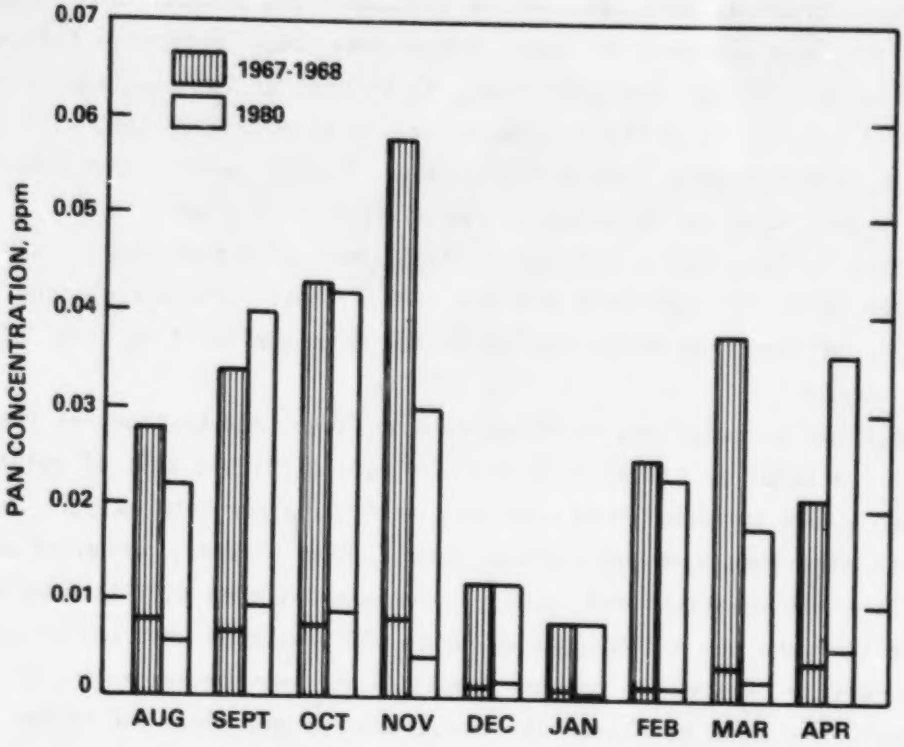

Figure 6-34. Comparison of monthly daylight average and maximum PAN concentrations at Riverside, CA, for 1967-1968 and 1980.

Source: Derived from Temple and Taylor (1983)

TABLE 6-17. RELATIONSHIP OF OZONE AND PEROXYACETYL NITRATE AT URBAN AND SUBURBAN SITES IN THE UNITED STATES

Site/year	PAN/O_3, % Avg.	PAN/O_3, % At O_3 peak	Reference
CALIFORNIA			
Downtown Los Angeles, 1960	8	7	Renzetti and Bryan (1961)
Downtown Los Angeles, 1965	NA	7	Mayrsohn and Brooks (1965)
Downtown Los Angeles, 1968	13	NA[a]	Lonneman et al. (1976)
West Los Angeles, 1980	9	6	Hanst et al. (1982)
Pasadena, 1973	10	8	Hanst et al. (1975)
West Covina, 1977	20	12	Spicer (1977)
Claremont, 1978	7	6	Tuazon et al. (1981a, 1981b)
Claremont, 1979	4	4	Tuazon et al. (1981a)
Riverside, 1967-1968	8	NA[a]	Taylor (1969)
Riverside, 1975-1976	9	5	Pitts and Grosjean (1979)
Riverside, 1976	5	4	Tuazon et al. (1978)
Riverside, 1977	4	4	Tuazon et al. (1980)
Riverside, 1977	4	NA[a]	Singh et al. (1979)
SOUTHWEST			
Houston, TX, 1976	3	3	Westberg et al. (1978)
MIDWEST			
St. Louis, MO, 1973	13	NA[a]	Lonneman et al. (1976)
St. Louis, MO, 1973	5	5	Spicer (1977)
Dayton, OH, 1974 (Huber Hts, OH)	2	1	Spicer et al. (1976)
EAST			
Hoboken, NJ, 1970	4	NA[a]	Lonneman et al. (1976)
New Brunswick, NJ 1978-1980	4	2	Brennan (1980)

[a] Not available.

Source: Adapted from Altshuller (1983).

The only homologue of PAN that has been unambiguously identified in ambient air in the United States is peroxypropionyl nitrate (PPN). In his review of existing literature, Altshuller (1983) compiled data on the concentrations of PPN in ambient air in urban areas. In addition, he calculated ratios of the concentrations of PPN and PAN. His data, modified to express ratios as percentages [(PPN/PAN) x 100], are presented as Table 6-18 (Altshuller, 1983).

As Altshuller has pointed out, average PPN concentrations are 10 to 30 percent of the average PAN concentrations in Table 6-18 except for San Jose (8 percent) and Oakland (42 percent). The maximum PPN concentrations reported are highly variable, however, ranging from 0.13 ppb in San Jose (August 1978) to 6.0 ppb in Riverside (month and year as well as sampling period of day unknown). Thus, the PPN/PAN ratio at maximum concentrations of PPN is highly variable, as well. Among more recent data, the maximum PPN concentration was 5.0 ppb in St. Louis in August 1973. (Note, however, that the sampling period in St. Louis was 10:00 a.m. to 3:30 p.m. Depending upon temperature and concentrations of precursors, a true PPN maximum may or may not have occurred by 3:30 p.m.)

A comparison of data in Table 6-19 obtained by the same investigators (Singh et al., 1981) for three separate cities (Los Angeles, Oakland, and Phoenix) helps demonstrate the variability of PPN and PAN concentrations between locations. Table 6-19 is derived from Singh et al. (1981) and presents PAN and PPN concentrations for the three cities, as well as PPN/PAN ratios (in percent) calculated from their data.

6.6.4 Ambient Air Concentrations of PAN and Its Homologues in Nonurban Areas

Data on the concentrations of PAN and PPN in agricultural and other nonurban areas of the United States are sparse. They include the measurements done by Lonneman et al. (1976) in Wilmington, Ohio, in 1974, and by Westberg et al. (1978) in Downington, Pennsylvania, in 1979, two agriculturally-oriented areas. In the study by Lonneman et al. (1976), cited earlier in section 6.6.1, measurements made by GC-ECD from 10:00 a.m. to 4:00 p.m., local time, showed a maximum concentration for the study period of 4.1 ppb. The average daily maximum was 2.0 ppb. Westberg et al. (1978) measured PAN from 8:00 a.m. to 6:00 p.m. and found a maximum concentration for the study period of 5.0 ppb; the average daily maximum was 2.2 ppb and the average for the entire study period was <1 ppb. While the 4:00 p.m. cutoff used by Lonneman et al.

TABLE 6-18. AMBIENT AIR MEASUREMENTS OF PEROXYPROPIONYL NITRATE CONCENTRATIONS BY ELECTRON CAPTURE GAS CHROMATOGRAPHY AT URBAN SITES IN THE UNITED STATES

Site	Period of measurement/ no. of days (n)	Period of day	Peroxypropionyl nitrate, ppb		(PPN/PAN, percent)		Reference
			Avg.	Max.	Avg.	Max.	
Los Angeles, CA	April 1979 (13)	24 hr	0.7	2.7	15	16	Singh et al. (1981)
Riverside, CA	NA[a] (1)	NA[a]	NA[a]	6	NA[a]	12	Darley et al. (1963)
Riverside, CA	April-May	24 hr	0.3	1.8	21	32	Singh et al. (1979)
Riverside, CA	July 1980 (13)	24 hr	0.2	0.9	16	16	Singh et al. (1981)
San Jose, CA	August 1978 (7)	24 hr	0.08	0.13	8	10	Singh et al. (1979)
Oakland, CA	June-July 1979 (13)	24 hr	0.15	0.5	28	42	Singh et al. (1981)
Phoenix, AZ	April-May 1979 (14)	24 hr	0.09	0.33	12	9	Singh et al. (1982)
Denver, CO	June 1980 (14)	24 hr	0.05	0.32	10	3	Singh et al. (1982)
Houston, TX	May 1980 (12)	24 hr	0.11	0.63	14	25	Singh et al. (1982)
St. Louis, MO	10 Aug. 1973 (1)	1000-1530 (LT[b])	3.0	5.0	17	20	Lonneman et al. (1976)
St. Louis, MO	May-June, 1980 (9)	24 hr	0.66	0.25	23	28	Singh et al. (1982)
Chicago, IL	April-May, 1981 (13)	24 hr	0.05	0.13	12	8	Singh et al. (1982)
Pittsburgh, PA	April 1981 (11)	24 hr	0.05	0.07	17	10	Singh et al. (1982)
Staten Island, NY	March-April 1981 (11)	24 hr	0.20	3.1	27	80	Singh et al. (1982)

[a] Not available.

[b] Local time.

Source: Altshuller (1983).

TABLE 6-19. CONCENTRATIONS OF PEROXYACETYL AND PEROXYPROPIONYL NITRATES IN LOS ANGELES, OAKLAND, AND PHOENIX, 1979 (ppb)

Value	Los Angeles			Oakland			Phoenix		
	PAN	PPN	PPN/PAN, %	PAN	PPN	PPN/PAN, %	PAN	PPN	PPN/PAN, %
Mean	4.977	0.722	14	0.356	0.149	42	0.779	0.093	12
Std. dev.	4.483	0.673	-	0.422	0.118	-	0.767	0.077	-
Maximum	16.820	2.740	16	1.850	0.500	27	3.720	0.330	9
Minimum	0.030	ND[a]	-	0.050	ND[a]	-	ND[a]	ND[a]	-

[a] Not detectable. Lower limit of detection is ~0.02 part per trillion (ppt) for PAN and ~0.03 ppt for PPN.

Source: Singh and Salas (1983).

(1976) could possibly have resulted in missing some peak PAN concentrations, especially in transported air masses, the data from that study are comparable to those of the Westberg et al. (1978) study, in which the sampling period extended to 6:00 p.m. (local time).

Data from two nonurban sites in Canada are of interest even though they are outside the United States. Cherniak and Corkum (1981; in Temple and Taylor, 1983) measured PAN at a nonurban site in Simcoe, Ontario, Canada for 6 months. Measurements made by GC-ECD showed monthly means of <2 ppb and a maximum concentration during the study of 5.6 ppb. At a remote site in the Kananaskis Valley of Alberta, Canada, monthly mean concentrations were <1 ppb for samples taken at half-hour intervals, 24 hr/day, for 110 days. The site, located at the base of a mountain range and about 50 miles west of Calgary, is thought to be free of manmade pollutants, including transported pollutants.

Concentrations of PAN have recently been reported by Singh and Salas (1983) for a Pacific marine site, Point Arena, California, at which earlier measurements were also made and reported by Singh et al. (1979) (see Table 6-20). Data collected in August 1982 showed concentrations of PAN ranging from 0.01 to 0.12 ppb during the 5-day study period. The average concentration for the period was 0.032 ± 0.024 ppb. The site is thought to be free of manmade pollutants. Winds were west-to-northwest 90 percent of the time and northerly the rest of the time. Modeled trajectories confirmed that air masses passing over the site were of a marine origin.

In his comprehensive review, Altshuller (1983) compiled data on PAN, PPN, and O_3 concentrations at nonurban sites in the United States. These data are presented in Table 6-20.

6.6.5 Temporal Variations in Ambient Air Concentrations of Peroxyacetyl Nitrate

6.6.5.1 Diurnal Patterns. Concentration data obtained in the 1960s were briefly discussed in section 6.6.1, where it was noted that the first criteria document for photochemical oxidants (U.S. Department of Health, Education, and Welfare, 1970) documented concentrations and patterns that remain valid now. In that document, the general proximity in time of PAN and oxidant peaks was established by data from Los Angeles and Riverside, California. Maximum PAN concentrations, although varying from location to location, generally occur in midday; i.e., late morning to mid-afternoon. Figures 6-35 and 6-36, taken from the 1970 criteria document (U.S. Department of Health, Education, and

TABLE 6-20. CONCENTRATIONS IN AMBIENT AIR OF PEROXYACETYL AND PEROXYPROPIONYL NITRATES AND OZONE AT NONURBAN REMOTE SITES IN THE UNITED STATES (ppb)

Site	Reference	Nature of site	Period of measurement and no. of days (n)	Period of day	Average concentrations			Maximum concentrations			Avg. PAN/ Avg. O_3, %
					PAN	PPN	O_3	PAN	PPN	O_3	
Mill Valley, CA	Singh et al. (1979)	Maritime	Jan. 1977 (12)	24 hr	0.30	0.04	38	0.83	0.11	0.55	0.8
Point Arena, CA	Singh et al. (1979)	Clean-maritime	Aug.-Sept. 1978 (7)	24 hr	0.08	ND[a]	ND[a]	0.28	ND[a]	ND[a]	ND[a]
Badger Pass, CA	Singh et al. (1979)	Remote-high altitude	May 1977 (10)	24 hr	0.13	0.05	46	0.22	0.09	54	0.3
Reese River, NV	Singh et al. (1979)	Remote-high altitude	May 1977 (7)	24 hr	0.11	0.04	39	0.26	0.09	56	0.3
Jetmore, KA	Singh et al. (1979)	Rural-continental	June 1978 (7)	24 hr	0.25	ND[a]	31	0.52	ND[a]	53	0.8
Sheldon Wildlife Reserve, TX	Westberg et al. (1978)	Rural-continental	October 1978 (9)	24 hr	0.64	ND[a]	47	2.8	ND[a]	148	1.4
Wilmington, OH	Lonneman et al. (1976)	Rural-continental	August 1974 (9)	24 hr	NA[b]	ND[a]	NA[b]	4.1	ND[a]	107	NA[b]
Van Hiseville, NJ	Spicer and Sverdrup (1981)	Rural-continental	July-Aug. 1979 (31)	24 hr	0.50	ND[a]	36	6.5	ND[a]	161	1.4

[a] Not determined.

[b] Measured, but results not given in the reference.

Source: Altshuller (1983).

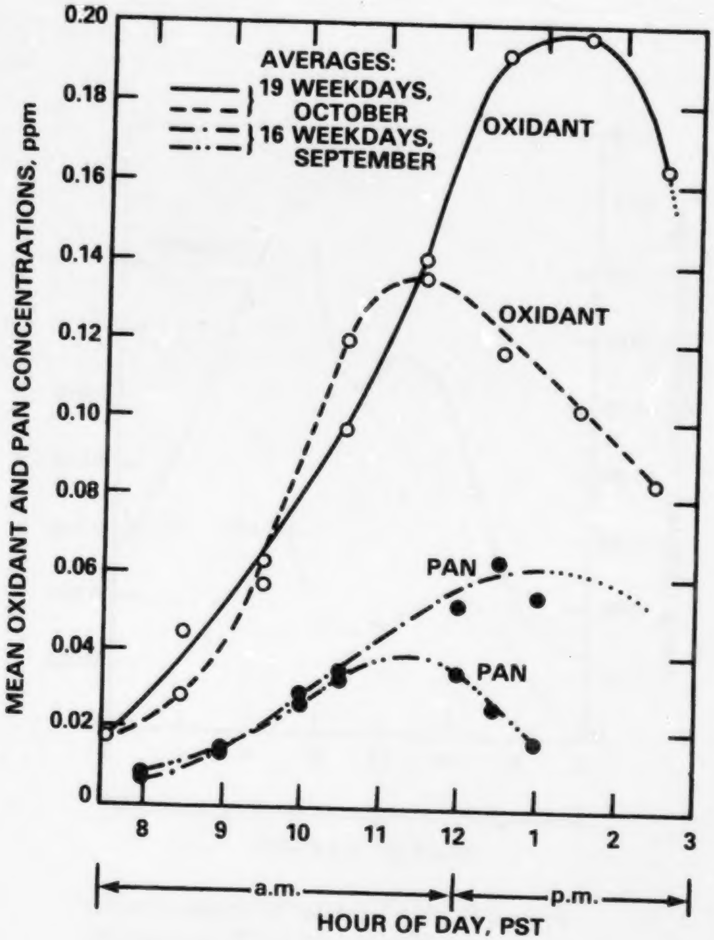

Figure 6-35. Variation of mean 1-hour oxidant and PAN concentrations, by hour of day, in downtown Los Angeles, 1965.

Source: U.S. Department of Health, Education, and Welfare (1970)

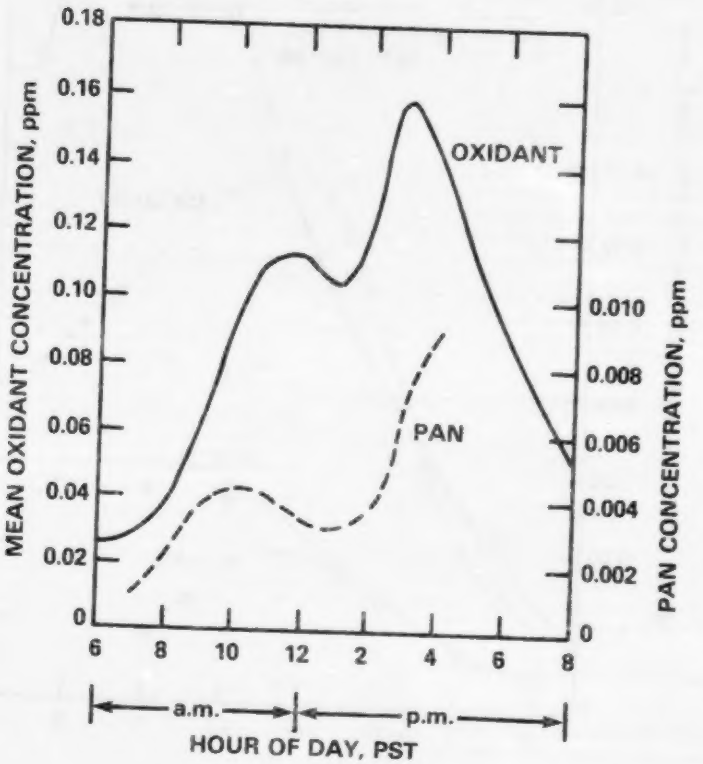

Figure 6-36. Variation of mean 1-hour average oxidant and PAN concentrations by hour of day, Air Pollution Research Center, Riverside, CA, September 1966.

Source: U.S. Department of Health, Education and Welfare (1970)

Welfare), graphically present the diurnal patterns of PAN in Los Angeles in 1965 and in Riverside in 1966. The occurrence of the second PAN peak in Riverside, which appears to trail a second total oxidant peak by an hour or two, was ascribed to transport, as verified by the occurrence of maximum oxidant concentrations at three receptor sites east of West Los Angeles (downtown Los Angeles, Azusa, and Riverside), at times that corresponded with respective distances from West Los Angeles.

Two examples drawn from recent data substantiate that the general diurnal pattern (as it appears in composite diurnal data averaged over a week, a month, or longer) remains the same as the pattern established by data obtained in the mid-1960s.

Using FTIR spectroscopy, Tuazon and coworkers (Tuazon et al., 1978, 1980, 1981b) measured concentrations of PAN at Claremont and Riverside over a 5-year period. Concentrations of PAN ranged from about 5 to 40 ppb over the course of the study. The diurnal profiles for PAN and ozone at Claremont are shown for 2 days of a multi-day smog episode in October 1978 in Figure 6-37 (Tuazon et al., 1981b). Note the qualitative relationship of the two pollutants, in which the peak concentrations of the two occur almost simultaneously. That the relationship between PAN and ozone concentrations and behavior in the atmosphere is neither constant nor monotonic is borne out by the slight time differences in occurrence of their peak concentrations but especially by the persistence of somewhat elevated PAN concentrations before return to "baseline" levels. It appears that PAN concentrations, in this instance at least, closely parallel the nitric acid (HNO_3) concentrations, persisting after ozone concentrations have subsided. The quantitative relationship between PAN and ozone differed slightly at the peak concentrations of the two on the 2 days. On October 12, the peak PAN concentration was close to 6 percent of the peak ozone concentration; on October 13, the peak PAN concentration was nearly 8 percent of the peak ozone concentration.

6.6.5.2 Seasonal Patterns. Seasonal differences in PAN concentrations were alluded to in section 6.6.3 and mean and maximum PAN concentrations were presented by month for 2 years (1967-1968 and 1980) for Riverside, California, in Figure 6-34. That seasonal differences exist in PAN concentrations was documented in the 1970 criteria document for photochemical oxidants (U.S. Department of Health, Education, and Welfare, 1970). Oxidant data for the same period were obtained by continuous Mast meter measurements, 24 hr/day. Concentrations

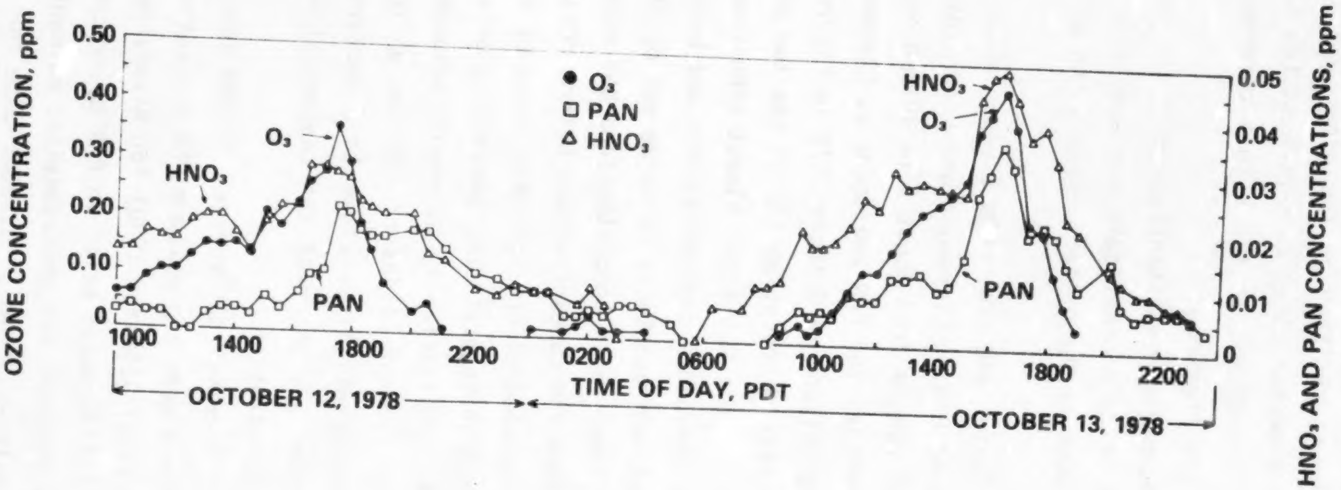

Figure 6-37. Diurnal profiles of ozone and PAN at Claremont, CA, October 12 and 13, 1978, 2 days of a multi-day smog episode.

Source: Tuazon et al. (1981)

of PAN were measured in sequential samples analyzed by GC-ECD from 6:00 a.m. to about 4:00 or 5:00 p.m. The data are not strictly comparable, since the shorter, daylight averaging time for PAN would be expected to result in somewhat higher mean concentrations of PAN than would be obtained across a 24-hour averaging period. Nevertheless, the patterns, given in Figure 6-38, are of interest and demonstrate that peak PAN concentrations can constitute a higher percentage of the peak ozone concentrations during winter months than during the rest of the year. This observation is still valid (Spicer et al., 1983) and has been attributed by Holdren et al. (1984) to greater stability in the winter months because of cooler temperatures (Cox and Roffey, 1977). The possibility that the somewhat greater NO_x emissions of the heating season (winter months) may contribute to this phenomenon should not be overlooked.

Data from one additional study complement data already presented on diurnal and seasonal patterns. Lewis et al. (1983) measured PAN and ozone concentrations from September 25, 1978, to May 10, 1980. Average (10-hr and 24-hr) and maximum concentrations of both pollutants are given in Table 6-21 by month of the year (Lewis et al., 1983). Note that the highest monthly mean concentrations, both 10-hr and 24-hr, occurred during the smog season (August and September) but that the next highest occurred in October and February, respectively. Average diurnal profiles were obtained during this same study and are shown, by month, in Figure 6-39 (Lewis et al., 1983).

6.6.6 Spatial Variations in Ambient Air Concentrations of Peroxyacetyl Nitrate

6.6.6.1 Urban-Rural Gradients and Transport of PAN. Whether PAN, like ozone, can be transported from urban to rural areas is of consequence in assessing potential exposures of crops in agricultural areas. As noted earlier, precursors to PAN, especially NO_2, are lower in nonurban than in urban areas, such that little local formation is expected in nonurban areas. Available data on PAN concentrations indicate clearly that they are lower in nonurban areas than in urban (section 6.5.3). It should be noted, however, that data on concentrations in agricultural areas are quite sparse, such that the possibility of transport is important in assessing exposures of vegetation, especially since PAN is a known phytotoxicant. Studies by Lonneman et al. (1976) and Nieboer and Van Ham (1976) that were cited in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) reported the transport of PAN. The more recent study by Nielsen et al. (1982) has confirmed that PAN can be present at relatively

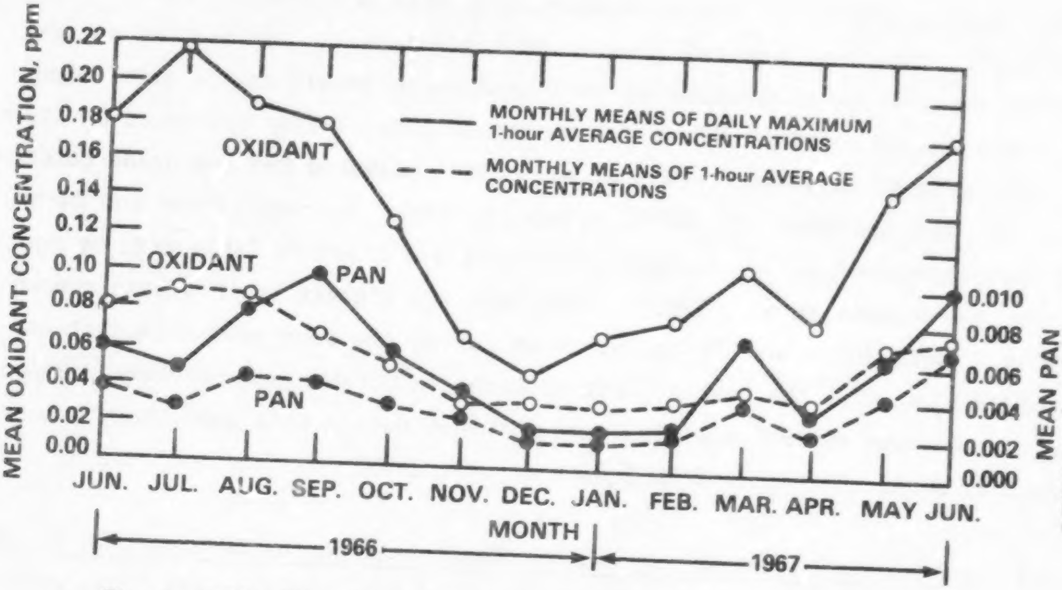

Figure 6-38. Monthly variation of oxidant (Mast meter, continuous 24-hr) concentrations and PAN (GC-ECD, sequential, 6:00 a.m. to 4:00-5:00 p.m.) concentrations, Air Pollution Research Center, Riverside, CA, June 1966 - June 1967.

Source: U.S. Department of Health, Education, and Welfare (1970)

TABLE 6-21. PAN AND OZONE CONCENTRATIONS IN AMBIENT AIR, NEW BRUNSWICK, N.J., FOR SEPTEMBER 25, 1978, TO MAY 10, 1980

Month	PAN concentration, ppb 24-hr average	PAN concentration, ppb 10-hr average	PAN concentration, ppb Hourly maximum	O_3 concentration, ppb 24-hr average	O_3 concentration, ppb 10-hr average	O_3 concentration, ppb Hourly maximum
January	0.12	0.19	1.3	11.5	15.5	34
February	0.61	0.69	4	17.2	23.2	40
March	0.36	0.41	1.3	23	29.1	58
April	0.45	0.57	2.5	28.5	37.3	80
May	0.23	0.28	1	31.4	40.9	78
June[a]	0.09	0.17	0.8	NA	NA	NA
July	0.26	0.44	3.5	37.5	57.6	130
August	1.17	1.63	10.6	37.4	55.9	145
September	1.04	1.41	7.5	22.4	33.9	110
October	0.93	1.08	5.8	15.8	22.6	68
November	0.25	0.31	3.5	11.6	15.8	40
December	0.57	0.62	2.5	9.7	12.8	35

[a] These results are lower than expected; however, there was no evidence of instrument malfunction.

Source: Lewis et al. (1983).

high concentrations in photochemically polluted air after long-range transport. Variations in concentrations of PAN and other oxidants measured in Claremont, California (Grosjean, 1983), are consistent with transport patterns. Recent work of Singh and Salas (1983) has shown that significant nighttime PAN concentrations can occur aloft, at least in a relatively clean environment. It is possible that the transport of PAN occurs aloft, as with ozone, and that it can be transported long distances under the right conditions.

6.6.6.2 Intracity Variations. Few data on PAN concentrations at different sites in the same city are available. One study is available for Houston, Texas (Jorgen et al., 1978), in which PAN was measured on October 26 and 27, 1977, at three separate sites, two within Houston and one just north of the city. Diurnal concentration plots for the three sites are shown as Figures 6-40 through 6-42. Site 2 was in Houston, near the junction of routes I-10 and I-45. Site 3 was located about 11 miles south-southeast of site 2; site 1 was about 12 miles north and slightly east of site 2; and sites 1 and 3 were about 22 miles apart.

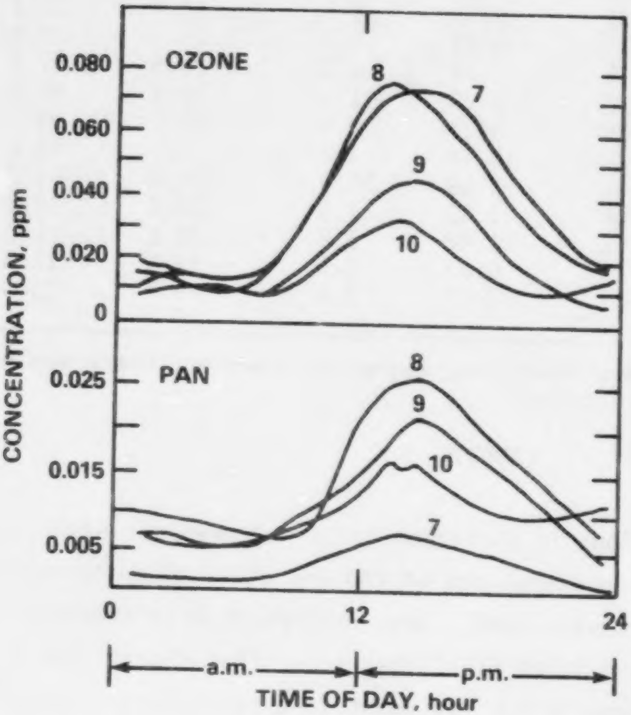

Figure 6-39. Average daily profile by month (July 7 - October 10) for PAN and ozone in New Brunswick, NJ, 1979. Numbers refer to months of the year.

Source: Lewis et al. (1983)

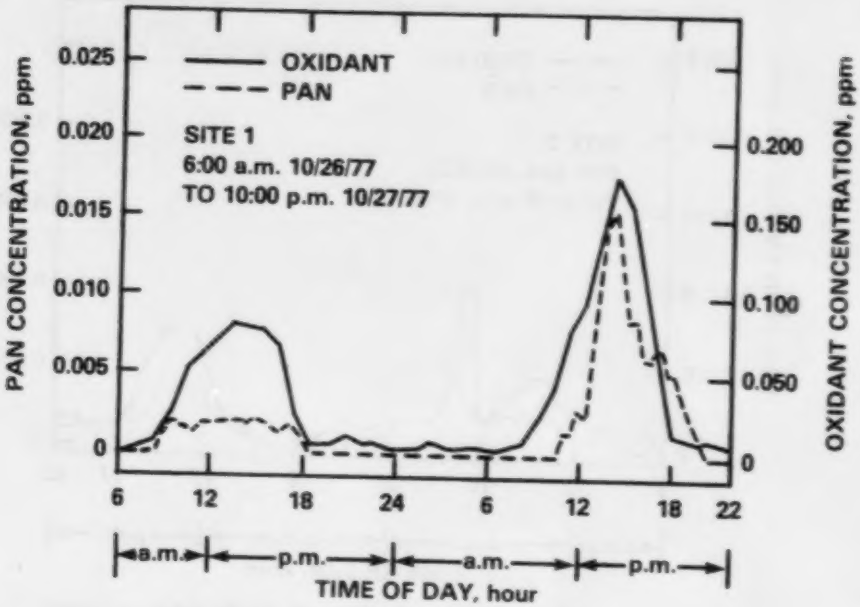

Figure 6-40. Diurnal plot of PAN and oxidant concentrations at site just north of Houston, October 26-27, 1977.

Source: Jorgen et al. (1977)

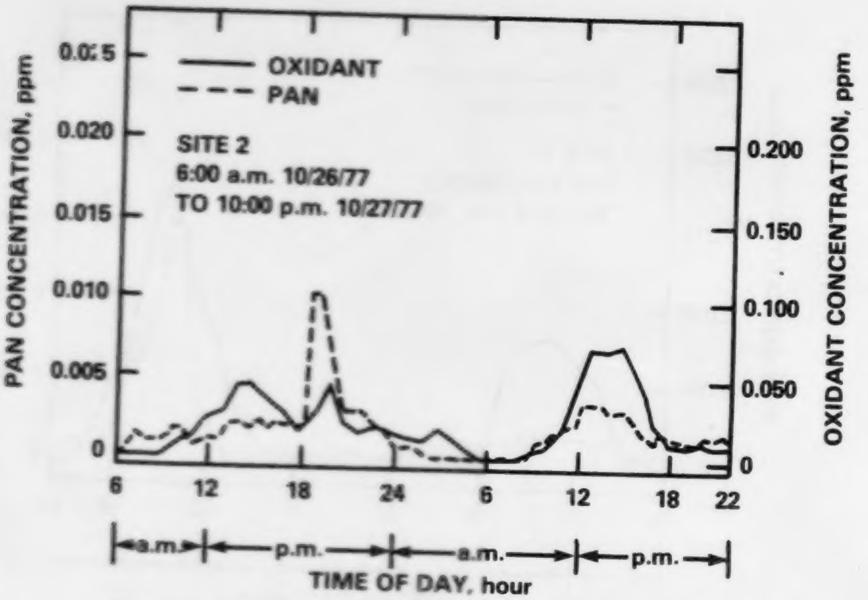

Figure 6-41. Diurnal plot of PAN and oxidant concentrations at site in Houston, near junction of I-10 and I-45, October 26-27, 1977.

Source: Jorgen et al. (1978)

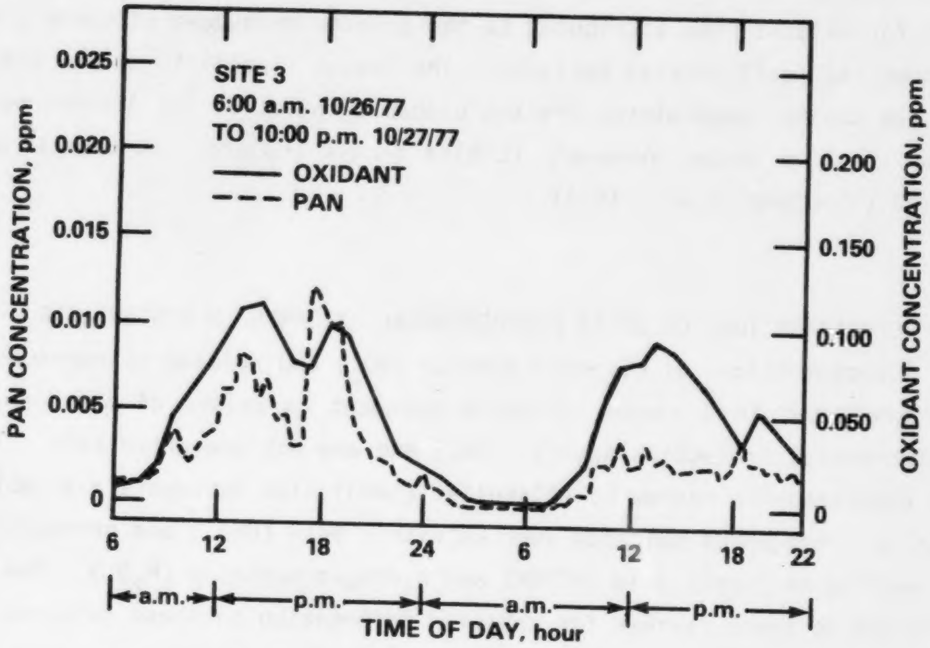

Figure 6-42. Diurnal plot of PAN and oxidant concentrations at site in Southeast Houston, October 26-27, 1977.

Source: Jorgen et al. (1978)

6.6.6.3 Indoor-Outdoor Ratios of PAN Concentrations.

No recent studies appear in the literature on indoor concentrations of PAN or indoor-outdoor ratios (I/O). In three school buildings in southern California, Thompson et al. (1973) found I/O ratios (expressed here as percentages) of 89, 97, and 148 percent, respectively, in the absence of air conditioning. With air conditioning, the I/O ratios were 75, 108, and 117 percent, respectively. Total oxidants were nearly constant all day, remaining about 30 percent (in air conditioning) of the average outside concentration. The higher I/O for PAN than for oxidants was attributed to the greater breakdown of ozone ("oxidants") through its reaction with surfaces. The lesser reactivity of PAN with surfaces and the cooler temperatures are the probable causes of its greater persistence indoors. Like ozone, however, it also decays indoors, but over an extended period (Thompson et al., 1973).

6.7 CONCENTRATIONS OF OTHER PHOTOCHEMICAL OXIDANTS IN AMBIENT AIR

Concentrations of nitrogen dioxide (NO_2) and related nitrogenous oxidants are presented in a recent criteria document on oxides of nitrogen (U.S. Environmental Protection Agency, 1982) and are not presented here. In addition, the comprehensive review by Altshuller (1983) also documents available information on nitrogenous oxidants such as nitric acid (HNO_3) and peroxynitric acid, as well as on formic acid (HCOOH) and hydrogen peroxide (H_2O_2). The reader is referred to these reviews for detailed information on these oxidants. Because formic acid and hydrogen peroxide are appropriate concerns for this document, however, the limited information on concentrations of these two pollutants is summarized below.

Neither health nor welfare effects have ever been attributed to the presence of formic acid in ambient air. It has been found in polluted areas such as the Los Angeles Basin at concentrations up to 20 ppb. Maximum concentrations of HCOOH observed by Tuazon and coworkers, using FTIR (Tuazon et al., 1978; 1980; 1981b), in Claremont and Riverside were in the range 5 to 20 ppb in a study covering 5 years. The ranges of concentrations of HCOOH measured by Tuazon et al. were consistent with those found in a recent long-path FTIR study by Hanst et al. (1982). The FTIR method offers a reliable assessment of the ambient air concentrations of HCOOH and reported concentrations are believed to be accurate.

Data on HCOOH concentrations for 2 days in October 1978 are shown in Figure 6-43 (Tuazon et al., 1981b). The diurnal pattern is similar to that of related oxidants and of some of the other smog products.

The measurement of hydrogen peroxide (H_2O_2) in ambient air is fraught with difficulties that remain unresolved. Ozone itself is known to be an interference in virtually all of the past and current measurement methods for H_2O_2 (chapter 5). In his comprehensive review of non-ozone oxidants and other smog constituents and photochemical products, Altshuller (1983) examined data obtained in the South Coast Air Basin of California in the late 1970s and in 1980 for possible consistency in the interference of ozone in H_2O_2 measurements. Laboratory experiments (Heikes et al., 1982) have indicated that 1 ppb H_2O_2 would be generated per 100 ppb ozone. Altshuller's analysis shows that this relationship does not hold in ambient air in the South Coast Air Basin once H_2O_2 levels exceed about 5 to 10 ppb, and Altshuller (1983) concluded that variations in H_2O_2 measurements there remain unexplained.

Because of measurement problems, the true levels of H_2O_2 in ambient air are unknown, especially in polluted areas, where multiple interferences may possibly occur. The FTIR method has been used to look for hydrogen peroxide in ambient air, but concentrations, even in polluted areas, are apparently below the limits of detection of the method; FTIR spectroscopy is known to be capable of measuring H_2O_2 with specificity if it is present above the limits of detection (40 ppb at 1 km pathlength; see chapter 5).

Notwithstanding measurement difficulties, some ranges of H_2O_2 concentrations at urban and nonurban sites have been reported in the literature. These are given in Table 6-22, along with the general type of measurement method used to obtain the reported concentrations. It must be kept in mind, however, that the reported concentrations are not thought to be accurate but to be rough approximations only of H_2O_2 levels in ambient air.

6.8 SUMMARY

In the context of this document, the concentrations of ozone and other photochemical oxidants found in ambient air are important for:

1. Assessing potential exposure of individuals; communities; the general population and those subpopulations in communities that may be especially susceptible to adverse effects from these oxidants; natural ecosystems, managed ecosystems such as crops; and nonbiological materials such as polymers and paints.

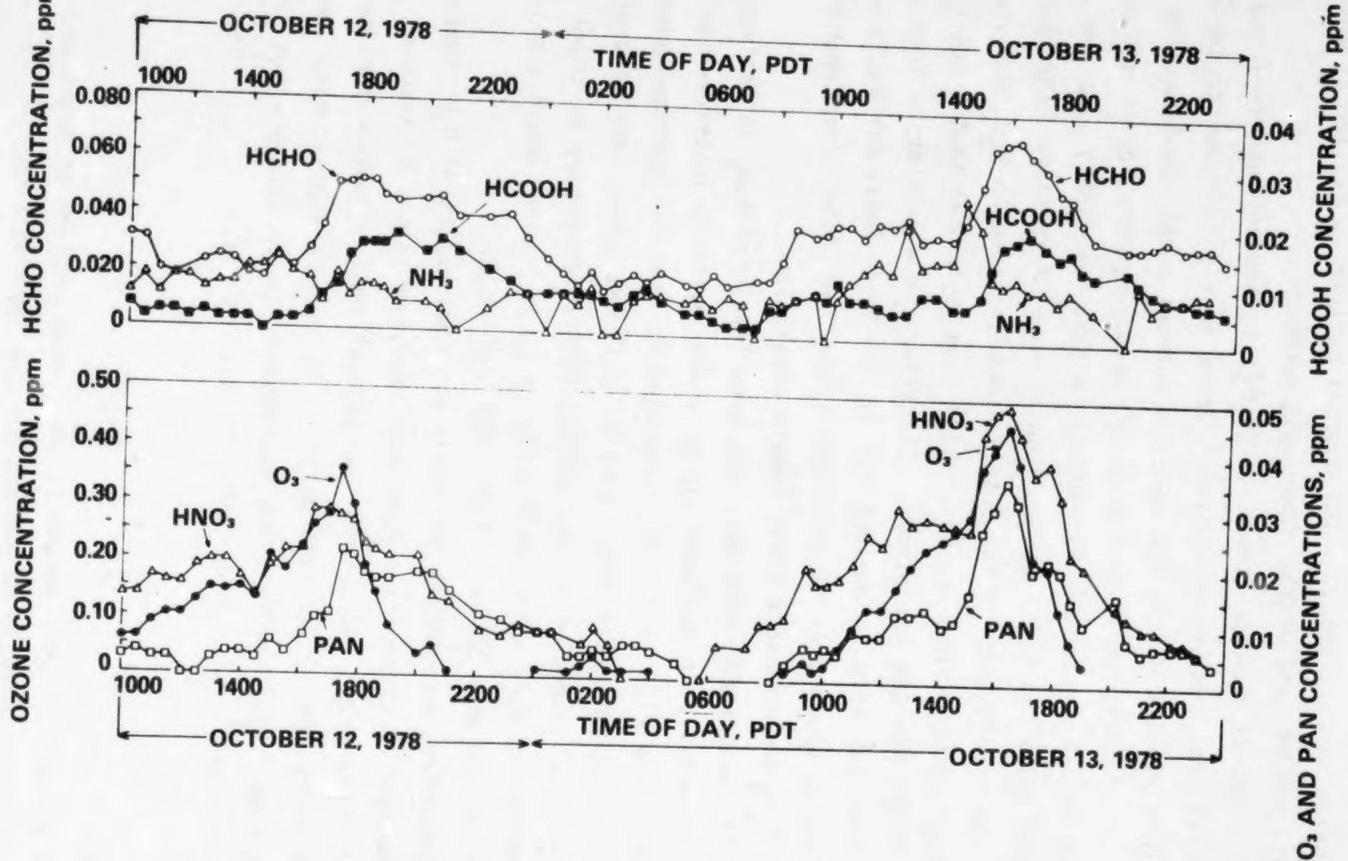

Figure 6-43. Diurnal profile of HCOOH, along with other oxidants and smog constituents, on October 12 and 13, 1978, at Claremont, CA.

Source: Tuazon et al. (1981b).

TABLE 6-22. CONCENTRATIONS OF HYDROGEN PEROXIDE IN AMBIENT AIR AT URBAN AND NONURBAN SITES

Location	Date	Concns., ppb; comments	Method	Reference
Hoboken, NJ (urban)	1970	$\leq$ 40	Titanium (IV) sulfate/8-quinolinol	Bufalini et al. (1972)
Riverside, CA (urban)	1970	$\leq$180 (during smog episode with 650 ppb oxidants)	Titanium (IV) sulfate/8-quinolinol	Bufalini et al. (1972)
Riverside and Claremont, CA (urban)	July-Aug 1977	100 max. (ozone also 100 and increasing); 10 to 50 on most days	Luminol chemiluminescence	Kok et al. (1978)
Minneapolis, MN (urban)	NA[a]	$\leq$6	Wet chemical[b]	Heikes et al. (1982)
Boulder, CO (urban)	NA[a]	$\leq$0.5	Wet chemical[b]	Heikes et al. (1982)
Boulder, CO (nonurban, east of Boulder)	Feb. 1978	0.2 to 3	Luminol chemiluminescence	Kelly et al. (1979)
Tucson, AZ (nonurban, 54 km SE of Tucson)	NA[a]	$\leq$7	Luminol chemiluminesence	Farmer and Dawson (1982)
Tucson, AZ (remote, near Tucson)	NA[a]	~1	Luminol chemiluminescence	Farmer and Dawson (1982)

[a] Not available from Altshuller (1983).

[b] See chapter 5 for method used by Heikes et al. (1982).

Source: Derived from data in Altshuller (1983).

2. Assessing whether levels of ozone and other photochemical oxidants in ambient air are within or near the range of concentrations shown to produce adverse effects in health and welfare effects studies.

3. Determining whether levels of ozone and other photochemical oxidants are as high indoors as in the ambient air, for the purpose of assessing actual, as opposed to potential, exposures of individuals in the general population or susceptible subpopulations.

4. Assessing whether non-ozone photochemical oxidants occur in ambient air at levels within or near the range of concentrations shown to produce potentially adverse effects in health and welfare effects studies.

5. Assessing whether concentrations of ozone plus the other photochemical oxidants together occur at levels sufficient to produce adverse effects in the general or susceptible subpopulations, or in vegetation and ecosystems.

6. Evaluating the relationship(s) between ozone and the other photochemical oxidants, in order to determine whether ozone can function as a control surrogate in the event that these other, non-ozone photochemical oxidants are found to produce adverse effects on public health and welfare.

6.8.1 Ozone Concentrations in Urban Areas

The current ozone standard is expressed in terms of a 1-hour value not to be exceeded on more than 1 day per year. Thus, the second-highest value is a concentration of significance, since it determines compliance with the standard and is, thereby, an indicator of exposures having potential health and welfare significance.

In this chapter, the second-highest 1-hour ozone concentrations reported in each of 4 years have been given for the 80 most populous Standard Metropolitan Statistical Areas (SMSAs) of the United States, i.e., those with populations $\geq$ 0.5 million. In Table 6-19, 1982 ozone concentrations for the subset of SMSAs with populations $\geq$ 1 million are given by geographic area, demarcated according to United States Census divisions and regions (U.S. Department of Commerce, 1982). The second-highest concentrations measured in 1982 in those 38 SMSAs having populations of at least 1 million ranged from 0.09 ppm in the Ft. Lauderdale, Florida, and Seattle, Washington, areas to 0.32 ppm in the Los Angeles and Riverside, California, areas. The second-highest 1-hour ozone concentrations for 32 of the 38 SMSAs in Table 6-19 equal or exceed 0.12 ppm.

TABLE 6-23. SECOND-HIGHEST 1-HR OZONE CONCENTRATIONS IN 1982 IN STANDARD METROPOLITAN STATISTICAL AREAS WITH POPULATIONS ≥ 1 MILLION, GIVEN BY CENSUS DIVISIONS AND REGIONS[a]

Division and region	SMSA	SMSA population, millions	Second-highest 1982 O_3 concn., ppm
NORTHEAST			
New England	Boston, MA	>2	0.16
Middle Atlantic	Buffalo, NY	1 to <2	0.11
	Nassau-Suffolk, NY	>2	0.13
	Newark, NJ	1 to <2	0.17
	New York, NY/NJ	>2	0.17
	Philadelphia, PA/NJ	>2	0.18
	Pittsburgh, PA	>2	0.14
SOUTH			
South Atlantic	Atlanta, GA	>2	0.14
	Baltimore, MD	>2	0.14
	Ft. Lauderdale-Hollywood, FL	1 to <2	0.09
	Miami, FL	1 to <2	0.14
	Tampa-St. Petersburg, FL	1 to <2	0.11
	Washington, DC/MD/VA	>2	0.15
SOUTH			
West South Central	Dallas-Ft. Worth, TX	>2	0.17
	Houston, TX	>2	0.21
	New Orleans, LA	1 to <2	0.17
	San Antonio, TX	1 to <2	0.14
NORTH CENTRAL			
East North Central	Chicago, IL	>2	0.12
	Detroit, MI	>2	0.16
	Cleveland, OH	1 to <2	0.12
	Cincinnati, OH/KY/IN	1 to <2	0.13
	Milwaukee, WI	1 to <2	0.13
	Indianapolis, IN	1 to <2	0.12
	Columbus, OH	1 to <2	0.13
West North Central	St. Louis, MO/IL	>2	0.15
	Minneapolis-St. Paul, MN/WI	>2	0.10
	Kansas City, MO/KS	1 to <2	0.10

TABLE 6-23 (cont'd). SECOND-HIGHEST 1-HR OZONE CONCENTRATIONS IN 1982 IN STANDARD METROPOLITAN STATISTICAL AREAS WITH POPULATIONS ≥ 1 MILLION GIVEN BY CENSUS DIVISIONS AND REGIONS[a]

Division and region	SMSA	SMSA population, millions	Second-highest 1982 O_3 concn., ppm
WEST			
Mountain	Denver-Boulder, CO	1 to <2	0.14
	Phoenix, AZ	1 to <2	0.12
Pacific	Los Angeles-Long Beach, CA	>2	0.32
	San Francisco-Oakland, CA	>2	0.14
	Anaheim-Santa Ana-Garden Grove, CA	1 to <2	0.18
	San Diego, CA	1 to <2	0.21
	Seattle-Everett, WA	1 to <2	0.09
	Riverside-San Bernardino-Ontario, CA	1 to <2	0.32
	San Jose, CA	1 to <2	0.14
	Portland, OR/WA	1 to <2	0.12
	Sacramento, CA	1 to <2	0.16

[a] Standard Metropolitan Statistical Areas and geographic divisions and regions as defined by Statistical Abstract of the United States (U.S. Department of Commerce, 1982).

Source: U.S. Environmental Protection Agency, SAROAD data file for 1982.

The data clearly show, as well, that the highest 1-hour ozone concentrations in the United States occur in the northeast (New England and Middle Atlantic States), in the Gulf Coast area (West South Central states), and on the west coast (Pacific states). Second-highest 1-hour concentrations in the SMSAs within each of these three areas average 0.15, 0.17, and 0.19 ppm, respectively. It should be emphasized that these three areas of the United States are subject to those meteorological and climatological factors that are conducive to local oxidant formation, or transport, or both. It should also be emphasized that 11 of the 16 SMSAs in the country with populations ≥ 2 million are located in these areas.

Sources of oxidant precursors are strongly correlated with population (chapter 3). In accord with this relationship, three population groups within the 80 largest SMSAs (Table 6-6) had the following median values for their collective second-highest 1-hour ozone concentrations in both 1981 and 1982: populations ≥ 2 million, 0.15 ppm O_3; populations of 1 to 2 million, 0.13 ppm O_3; and populations of 0.5 to 1 million, 0.12 ppm O_3.

Among all stations reporting valid ozone data (≥ 75 percent of possible hourly values per year) in 1979, 1980, and 1981 (collectively, 906 station-years) in the United States, the median second-highest 1-hour ozone value was 0.12 ppm, and 5 percent of these stations reported second-highest 1-hour values ≥ 0.28 ppm (Figure 6-9).

A pattern of concern in assessing human physiological and vegetational responses to ozone is the occurrence of repeated or prolonged periods, or both, when the ozone concentrations are close to or equal or exceed levels known to elicit responses. In addition, the number of days of respite between such multiple-day periods of high ozone is of possible consequence. Data presented in this chapter (Figures 6-23 through 6-26 and accompanying text) show that the probabilities of prolonged exposures to (consecutive days) or respites from (consecutive days) specified concentrations are location-specific. In Pasadena, CA, a high-ozone area, there is a 42 percent probability (based on 1979 through 1981 aerometric data) that an ozone concentration of 0.18 ppm, once reached, is likely to persist for 3 days or longer. Other, lower-ozone areas show lower probabilities of such multi-day high ozone concentrations. These and other data presented demonstrate the occurrence, at least in some urban areas, of multiple-day exposures to relatively high concentrations of ozone.

6.8.2. Trends in Urban and Nationwide Ozone Concentrations

Discussion in chapter 5 pointed out and substantiated that aerometric data obtained by potassium iodide methods in earlier years are essentially concentrations of ozone rather than "total oxidants." Comparison of concentrations of "total oxidants" in major urban areas for 1974 and 1975 in Table 6-2 (U.S. Environmental Protection Agency, 1978) with ozone data in Table 6-6 for those same urban areas in 1979 through 1982 (U.S. Environmental Protection Agency, SAROAD file) shows that the more recent ozone concentrations are in the same general range for many cities, have declined in some, and are somewhat higher in others.

Trends in nationwide ozone concentrations, gauged by annual averages at two subsets of stations reporting data from 1974 through 1981, show declines of 15 to 20 percent. These trend data represent urban areas almost exclusively. Interpretation of this trend is complicated by four potentially significant influences: (1) a change in calibration procedure (1979); (2) improved data-quality audits (1979); (3) possible shifts in underlying meteorological patterns; and (4) changes in precursor emission rates. When adjustments for the first two factors are made, a portion of the decrease is real. The exact portion of the decline that is attributable to the calibration change can not be determined without minute examination of aerometric data records from each monitoring station, since some monitoring stations began using the UV calibration procedure as early as 1975, some changed to UV calibration in 1979 (but not all in the same month of 1979), and some used the interim BAKI calibration procedure permitted by EPA for up to 18 months after promulgation of the UV calibration procedure (Hunt and Curran, 1982; also chapter 5).

6.8.3. Ozone Concentrations in Nonurban Areas

Nonurban areas are not routinely monitored for ozone concentrations. Consequently, the aerometric data base for nonurban areas is considerably less substantial than for urban areas. Data on maximum 1-hour concentrations and arithmetic mean 1-hour concentrations reveal that maximum (peak) 1-hour concentrations at nonurban sites classified as rural (SURE study, Martinez and Singh, 1979; NAPBN studies, Evans et al., 1983) may exceed the concentrations observed at nonurban sites classified as suburban (SURE study, Martinez and Singh, 1979). For example, maximum 1-hour ozone concentrations measured in 1980 at Kisatchie National Forest (NF), Louisiana; Custer NF, Montana; and Green Mt. NF, Vermont, were 0.105, 0.070, and 0.115 ppm, respectively. Arithmetic mean concentrations for 1980 were 0.028, 0.037, and 0.032 ppm at the respective sites. For four nonurban (rural) sites in the SURE study, maximum 1-hour ozone concentrations were 0.106, 0.107, 0.117, and 0.153; and mean 1-hour concentrations ranged from 0.021 to 0.035 ppm. At the five nonurban (suburban) sites of the SURE study, maximum concentrations were 0.077, 0.099, 0.099, 0.080, and 0.118 ppm, respectively. The mean 1-hour concentrations at those sites were 0.023, 0.030, 0.025, 0.020, and 0.025 ppm, respectively.

Comparison of these data with data for nonurban and remote locations during the 1973-1976 period show that mean concentrations at these various nonurban locations are not dissimilar. Ranges of concentrations and the maximum 1-hour concentrations at the NAPBN and SURE sites show the probable influence, however, of ozone transported from urban areas. In one documented case, for example, a 1-hour peak ozone concentration of 0.125 ppm at an NAPBN site in Mark Twain National Forest, Missouri, was measured during passage of an air mass whose trajectory was calculated to have included Detroit, Cincinnati, and Louisville in the preceding hours (Evans et al., 1983).

These data corroborate the conclusion given in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) regarding urban-nonurban and urban-suburban gradients; i.e., nonurban areas may sustain higher ozone concentrations than those found in urban areas. Reasons for this phenomenon include induction and transport times, as well as the possible additive effects of plumes from suburban or smaller areas as air masses pass over them downwind from urban areas. Generally, however, lower ozone concentrations occur in nonurban areas, as the data in this chapter indicate.

6.8.4. Patterns in Ozone Concentrations

Since the photochemical reactions of precursors that result in ozone formation are driven by sunlight, as well as emissions, the patterns of ozone occurrence in ambient air depend on daily and seasonal variations in sunlight intensity. The typical diurnal pattern of ozone in ambient air has a minimum ozone level around sunrise (near zero in most urban areas), increasing through the morning to a peak concentration in early afternoon, and decreasing toward minimal levels again in the evening. Obviously, meteorology is a controlling factor; if strong winds disperse the precursors or heavy clouds intercept the sunlight, high ozone levels will not develop. Another important variation on the basic diurnal pattern appears in some localities as a secondary peak in addition to the early afternoon peak. This secondary peak may occur any time from midafternoon to the middle of the night and is attributed to ozone transported from an upwind area where high ozone levels have occurred earlier in the day. As documented in this chapter, secondary peak concentrations may be higher than concentrations resulting from the photochemical reactions of locally emitted precursors (Martinez and Singh, 1979). At one nonurban site in Massachusetts, for example, primary peak concentrations of about 0.11, 0.14, and 0.14 occurred at noon, from noon to about 4:00 p.m., and at noon, respectively, on 3 successive days of high ozone levels (Martinez and Singh, 1979). Secondary peaks at the same site for those same 3 days were about 0.150, 0.157, and 0.130 ppm at about 6:00 p.m., 8:00 p.m., and 8:00 p.m., respectively (Martinez and Singh, 1979).

Because weather patterns, ambient temperatures, and the intensity and wavelengths of sunlight all play important roles in oxidant formation, strong seasonal as well as diurnal patterns exist. The highest ozone levels occur in the summer and fall (second and third quarters), when sunlight reaching the lower troposphere is most intense and stagnant meteorological conditions augment the potential for ozone formation and accumulation. Average summer afternoon levels can be from 150 to 250 percent of the average winter afternoon levels. Minor variations in the smog season occur with location, however. In addition, it is possible for the maximum and second-highest 1-hour ozone concentration to occur outside the two quarters of highest average ozone concentrations (cf. data for Tucson, Arizona, and data for the California sites given in this chapter). Exceptions to seasonal patterns are important considerations with regard to the protection of crops from ozone damage, especially since respective crops have different growing seasons in terms of length, time of year, and areas of the country in which they are grown.

As data in this chapter for different averaging times clearly demonstrate, averaging smooths out and submerges the occurrence of peak concentrations. This is an obvious and familiar statistical phenomenon. It is pointed out, however, because it has direct relevance to the protection of public health and welfare. Averaging times must correspond to or be related in a consistent manner to the pattern of exposure that elicits untoward responses.

Certain spatial variations in ozone concentrations occur that are generally of little consequence in exposure assessment. For example, ozone concentrations increase with increasing altitude (e.g., Viezee and Singh, 1981). The gradients are of no known consequence for inhabited elevations. They could potentially be of some consequence for high-altitude flights unless compensated for by adequate ventilation/filtration systems. Likewise, ozone concentrations exhibit hemispheric asymmetry (Logan et al., 1981), with concentrations highest in the northern hemisphere. Aerometric data sufficiently describe concentrations in the latitudes of the United States such that the fact of asymmetry has no practical consequences.

Spatial variations on a smaller scale assume more importance relative to exposure assessment. Indoor-outdoor gradients in ozone concentrations are known to occur even in structures ventilated by fresh air rather than air conditioning (e.g., Sabersky et al., 1973; Thompson et al., 1973). Ozone reacts with surfaces inside buildings, so that decay occurs fairly rapidly.

Ratios of indoor-to-outdoor (I/O) ozone concentrations are quite variable, however, since the presence or absence of air conditioning, air infiltration or exchange rates, interior air circulation rates, and the composition of interior surfaces all affect indoor ozone concentrations. Ratios (I/O) in the literature thus vary from 80 ± 10 percent (Sabersky et al., 1973) in an air-conditioned office building (but with 100 percent outside air intake) to 10 to 25 percent in air-conditioned residences (Berk et al., 1981).

On a larger scale, within-city variations in ozone concentrations can occur, despite the commonly accepted maxim that ozone is a regional pollutant. Data in this chapter show relatively homogeneous ozone concentrations in New Haven, Connecticut (U.S. Environmental Protection Agency, SAROAD files), which is a moderately large city downwind of a reasonably well-mixed urban plume (Cleveland et al., 1976). In a large metropolis such as New York City, however, appreciable gradients in ozone concentration can exist from one side of the city to the other (Smith, 1981). Such gradients must be taken into consideration in exposure assessments.

6.8.5 Concentrations and Patterns of Other Photochemical Oxidants

6.8.5.1 Concentrations. No aerometric data are routinely obtained by Federal, state, or local air pollution agencies for any photochemical oxidants other than nitrogen dioxide and ozone. The concentrations presented in this chapter for non-ozone oxidants were all obtained in special field investigations. The limitations in the number of locations and areas of the country represented in the information presented simply reflect the relative paucity of data in the published literature.

The four non-ozone photochemical oxidants for which concentration data have been presented are formic acid, peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and hydrogen peroxide. Peroxybenzoylnitrate has not been clearly identified in ambient air in the United States.

Recent data indicate the presence in urban atmospheres of only trace amounts of formic acid ($\leq$ 15 ppb, measured by FTIR). Estimates in the earlier literature (1950s) of 600 to 700 ppb of formic acid in smoggy atmospheres were erroneous because of faulty measurement methodology (Hanst et al., 1982).

The measurement methods (IR and GC-ECD) for PAN and PPN are specific and highly sensitive, and have been in use in air pollution research for nearly two decades. Thus, the more recent literature on the concentrations of PAN and PPN confirm and extend, but do not contradict, earlier findings reported in the two previous criteria documents for ozone and other photochemical oxidants (U.S. Department of Health, Education, and Welfare, 1970; U.S. Environmental Protection Agency, 1978).

Table 6-16 summarized the concentrations of PAN reported in the literature from 1960 through the present. The highest concentrations reported over this extended period were those found in the 1960s in the Los Angeles area: 70 ppb (1960), 214 ppb (1965); and 68 ppb (1968) (Renzetti and Bryan, 1961; Mayrsohn and Brooks, 1965; Lonneman et al., 1976; respectively).

The highest concentrations of PAN measured and reported in the past 5 years were 42 ppb at Riverside, California, in 1980 (Temple and Taylor, 1983) and 47 ppb at Claremont, California, also in 1980 (Grosjean and Kok, 1981). These are clearly the maximum concentrations of PAN reported for California and for the entire country in this period. Other recently measured PAN concentrations in the Los Angeles Basin were in the range of 10 to 20 ppb. Average concentrations of PAN in the Los Angeles Basin in the past 5 years ranged from 4 to 13 ppb (Tuazon et al., 1981a; Grosjean and Kok, 1981; respectively). Only one published report covering PAN concentrations outside California in the past 5 years is that of Lewis et al. (1983) for New Brunswick, New Jersey. The average PAN concentration was 0.5 ppb and the maximum was 11 ppb during a study done from September 1978 through May 1980. Studies outside California from the early 1970s through 1978 showed average PAN concentrations ranging from 0.4 ppb in Houston, Texas, in 1976 (Westberg et al., 1978) to 6.3 ppb in St. Louis, Missouri, in 1973 (Lonneman et al., 1976). Maximum PAN concentrations outside California for the same period ranged from 10 ppb in Dayton, Ohio, in 1974 (Spicer et al., 1976) to 25 ppb in St. Louis (Lonneman et al., 1976).

Table 6-18 summarized the findings of reports of PPN concentrations from 1963 through the present. The highest PPN concentration reported in these studies was 6 ppb in Riverside, California (Darley et al., 1963). The next highest reported PPN concentration was 5 ppb at St. Louis, Missouri, in 1973 (Lonneman et al., 1976). Among more recent data, maximum PPN concentrations at respective sites ranged from 0.07 ppb in Pittsburgh, Pennsylvania, in 1981 (Singh et al., 1982) to 3.1 ppb at Staten Island, New York (Singh et al., 1982). California concentrations fell within this range. Average PPN concentrations at the respective sites for the more recent data ranged from 0.05 ppb at Denver and Pittsburgh to 0.7 ppb at Los Angeles in 1979 (Singh et al., 1981).

Altshuller (1983) has succinctly summarized the nonurban concentrations of PAN and PPN by pointing out that they overlap the lower end of the range of urban concentrations at sites outside California. At remote locations, PAN and PPN concentrations are lower than even the lowest of the urban concentrations (by a factor of 3 to 4).

In urban areas, hydrogen peroxide (H_2O_2) concentrations have been reported to range from $\leq$ 0.5 ppb in Boulder, Colorado (Heikes et al., 1982) to $\leq$ 180 ppb in Riverside, California (Bufalini et al., 1972). In nonurban areas, reported concentrations ranged from 0.2 ppb near Boulder, Colorado, in 1978 (Kelly et al., 1979) to $\leq$ 7 ppb 54 km southeast of Tucson, Arizona (Farmer and Dawson, 1982). These nonurban data were obtained by the luminol chemiluminescence technique (see chapter 5). The urban data were obtained by a variety of methods, including the luminol chemiluminescence, the titanium (IV) sulfate 8-quinolinol, and other wet chemical methods (see chapter 5).

The higher concentrations of H_2O_2 reported in the literature must be regarded as especially problematic, since FTIR measurements of ambient air have not demonstrated unequivocally the presence of H_2O_2 even in the high-oxidant atmosphere of the Los Angeles area. The limit of detection for a 1-km-pathlength FTIR system is around 0.04 ppm (chapter 5); FTIR is capable of measuring concentrations of H_2O_2 if it is present above the limit of detection.

6.8.5.2 Patterns. The patterns of formic acid (HCOOH), PAN, PPN, and H_2O_2 may be summarized fairly succinctly. They bear qualitative but not quantitative resemblance to the patterns already summarized for ozone concentrations. Qualitatively, diurnal patterns are similar, with peak concentrations of each of these occurring in close proximity to the time of the ozone peak. The correspondence in time of day is not exact, but is close. As the work of Tuazon et al. (1981) at Claremont, California, demonstrates (see Figures 6-37 and 6-43), ozone concentrations return to baseline levels faster than the concentrations of PAN, HCOOH, or H_2O_2 (PPN was not measured). The diurnal patterns of PAN were reported in earlier criteria documents. Newer data merely confirm those patterns.

Seasonally, winter concentrations (third and fourth quarters) of PAN are lower than summer concentrations (second and third quarters). The winter concentrations of PAN are proportionally higher, however, than the winter concentrations of ozone. Data are not readily available on the seasonal patterns of the other non-ozone oxidants.

Indoor-outdoor data on PAN are limited to one report (Thompson et al., 1973), which confirms the pattern to be expected from the known chemistry of PAN; that is, it persists longer indoors than ozone. Data are lacking for the other non-ozone oxidants.

6.8.6 Relationship Between Ozone and Other Photochemical Oxidants

The relationship between ozone concentrations and the concentrations of PAN, PPN, H_2O_2, and HCOOH is important only if these non-ozone oxidants are shown to produce adverse health or welfare effects, singly, in combination with each other, or in various combinations with ozone. If only ozone is shown to produce adverse health or welfare effects, then only ozone needs to be controlled. If any or all these other four oxidants is shown to produce adverse health or welfare effects, then it, or they, will also have to be controlled. Since ozone and all four of the other oxidants arise from reactions among the same organic and inorganic precursors, an obvious question is whether the control of ozone will also result in the control of the other four oxidants.

Chapters 7 through 9 document what is known about the welfare effects of PAN. No data are available regarding the possible welfare effects of HCOOH, H_2O_2, or PPN. Chapters 10 through 13 document what is known about the health effects of PAN and H_2O_2. Formic acid is not covered because of extremely limited aerometric data and no health effects data pertinent to the trace quantities of formic acid measured in the ambient air. No health effects data are available for PPN. One report that PBzN is a potent lachrymator is not discussed in the health effects chapters since no reliable data indicate its presence in ambient air, even in high-oxidant areas. The health effects data reported in chapter 10 on H_2O_2 show that all levels tested to date are orders of magnitude above even the highest concentrations reported for ambient air; and, as noted above, the highest concentrations are not strongly documented. Thus, the brief discussion below focuses on the relationship between ozone and PAN concentrations in ambient air.

The most straightforward evidence of the lack of a quantitative, monotonic relationship between ozone and the other photochemical oxidants is the range of PAN-to-O_3 and, indirectly, of PAN-to-PPN ratios presented in the review of Altshuller (1983) and summarized in this chapter. Ratios of PAN concentrations to ozone concentrations are summarized in Table 6-17, derived from Altshuller (1983). The correspondence of PAN and ozone concentrations is not exact but is similar for most locations at which both pollutants have been measured in the same study. Disparities between locations point up the lack of a consistent quantitative relationship. Likewise, disparities between the ratio of the average concentrations of the two pollutants and the ratio of their concentrations when ozone is at its maximum level also point up the lack of a monotonically quantitative relationship.

Certain other information presented in this chapter bears out the lack of a monotonic relationship between ozone and PAN. Not only are ozone-PAN relationships not consistent between different urban areas, but they are not consistent in urban versus nonurban areas, in summer versus winter, in indoor versus outdoor environments, or even, as the ratio data show, in location, timing, or magnitude of diurnal peak concentrations within the same city. Data obtained in Houston by Jorgen et al. (1978) show variations in peak concentrations of PAN among three separate monitoring sites in the same city. Temple and Taylor (1983) have shown that PAN concentrations are a greater percentage of ozone concentrations in winter than in the remainder of the year in California (see chapter 6). Lonneman et al. (1976) demonstrated that PAN-to-O_3 ratios are considerably lower in nonurban than in urban areas. Thompson et al. (1973), in what is apparently the only published report on indoor concentrations of PAN, showed that PAN persists longer than ozone indoors. (This is to be expected from its lower reactivity with surfaces and its enhanced stability at cooler-than-ambient temperatures such as found in air-conditioned buildings.) Tuazon et al. (1981b) demonstrated that PAN persists in ambient air longer than ozone, its persistence paralleling that of nitric acid, at least in the locality studied (Claremont, CA). Reactivity data presented in the 1978 criteria document for ozone and other photochemical oxidants indicated that all precursors that give rise to PAN also give rise to ozone. The data also showed, however, that not all precursors giving rise to ozone also give rise to PAN. Not all that give rise to both are equally reactive toward both, however; and therefore some precursors preferentially give rise, on the basis of units of product per unit of reactant, to more of one product than the other (U.S. Environmental Protection Agency, 1978).

Altshuller (1983) prepared for the U.S. Environmental Protection Agency a comprehensive review and analysis of concentrations and relationships for ozone and other smog components, including PAN. The smog components he reviewed relative to ozone included aldehydes, aerosols, and nitric acid, as well as the non-ozone oxidants covered in this chapter. It must be emphasized that Altshuller examined the issue of whether ozone could serve as an abatement surrogate for all photochemical products, not just the subset of concern in this document. His conclusion was that "the ambient air measurements indicate that ozone may serve directionally, but cannot be expected to serve quantitatively, as a surrogate for the other products" (Altshuller, 1983). He found a greater correspondence between aldehydes and their organic precursors than between aldehydes and ozone. The correspondence between ozone and PAN concentrations (as well as PPN, H_2O_2, and HCOOH) is greater by far than the ozone-aldehyde relationship.

In summary, the significance for public health or welfare of the imposition of an additional oxidant burden from non-ozone oxidant rests on the answers to three basic questions:

1. Do PAN, PPN, H_2O_2, or HCOOH, singly or in combination, elicit adverse of potentially adverse responses?
2. Do any or all of these non-ozone oxidants act additively or synergistically in combination with ozone to elicit adverse or potentially adverse responses? Do any or all act antagonistically with ozone?
3. Do the time course magnitude of the concentrations of these non-ozone oxidants parallel the time course and magnitude of ozone concentrations in the ambient air?

Given the information on health and welfare effects presented in subsequent chapters, coupled with the aerometric data presented in this chapter, the relationship between ozone and PAN concentrations is the specific relationship of most concern in this document.

6.9 REFERENCES FOR CHAPTER 6

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